A STUDY TO DETERMINE THE CHEMICAL OXYGEN DEMAND CONCENTRATION AT WHICH NITRIFICATION BEGINS IN AN EXPERIMENTAL FIXED-BED REACTOR

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A STUDY TO DETERMINE THE CHEMICAL OXYGEN DEMAND CONCENTRATION AT WHICH NITRIFICATION BEGINS IN AN EXPERIMENTAL FIXED-BED REACTOR

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CHAPTER I

INTRODUCTION

Our modern urbanized and industrialized society now produces vast amounts of waterborne wastes each day. We are now faced with the ominous decision either to perform effective treatment upon our wastewater, or watch the environment and man's quality of life become further degraded by pollution. In order to meet the higher demands for pollution abatement, a more sophisticated technology must continuously develop.

A current higher demand that is the subject of ongoing research is the removal of ammonia (NH_4) from wastewater. This compound is the product of the decomposition of proteinaceous materials and is a common constituent of feedlot and municipal wastes. The concentration of nitrogen as ammonia in raw domestic wastewater may be found in a range from 12 to 50 mg/l (1). Ammonia can be toxic to fish in concentrations greater than 2.5 mg/l, and can exert a nitrogenous oxygen demand (NOD) upon a receiving watercourse. NOD can be attributed to lowering the dissolved oxygen content of the watercourse, thus endangering life of aquatic fauna and overall stream quality. Ammonia also increases chlorine or ozone demand required for disinfection of wastewater effluents. Several methods have been developed to remove ammonia from wastewater, including ammonia stripping, ion exchange, chemical oxidation, demineralization processes (electrodialysis, reverse osmosis,

and distillation), electrochemical treatment, land application, algae harvesting, bacterial assimilation, and nitrification-denitrification.

The nitrification-denitrification process involves aerobic microbial conversion of ammonia to nitrate (NO_3) during nitrification; then the nitrate is converted to nitrogen gas by an anaerobic microbial process (denitrification). This method has the advantage of returning the ammonia nitrogen to the atmosphere in its natural form. Sawyer (2) has stated that removal through nitrification followed by denitrification represents the most promising method at this time. McCarty (3) states the reasons for this method's appeal are 1) high potential removal efficiency, 2) process stability and reliability, 3) easy process control, 4) land area requirements, and 5) moderate costs. Nitrification alone will remove ammonia nitrogen, but the resulting nitrite and nitrate nitrogen will not be removed and can serve as nutrients for undesirable algal growths in surface waters. However, nitrification alone can help to eliminate ammonia toxicity to fish and will lower the chlorine demand and the NOD of a wastewater caused by the more reduced ammonia-nitrogen. It is important to note that denitrification will occur only upon the oxidized states of nitrogen. Therefore, the entire N-D process is dependent upon effective nitrification. In order to ensure complete denitrification, the nitrification must also be complete (4).

During the nitrification process, the ammonia is converted into nitrate in two steps by chemoautotrophic bacteria. These microorganisms use CO_2 as a source of carbon for cell material, and obtain energy by oxidizing the nitrogen-containining compounds.

Step 1:

$$NH_4^+ + 3/2\ O_2 \longrightarrow NO_2^- + 2H^+ + H_2O \text{ by } \underline{\text{Nitrosomonas}}$$

Step 2:

$$NO_2^- + 1/2\ O_2 \longrightarrow NO_3^- \text{ by } \underline{\text{Nitrobacter}}$$

Overall Energy Reaction:

$$NH_4^+ + 2\ O_2 \longrightarrow NO_3^- + 2H^+ + H_2O$$

Along with obtaining energy, however, some of the ammonium ion is assimilated into cell tissue. A representative synthesis reaction for this autotrophic has been suggested by McCarty (3).

Synthesis:

$$4\ CO_2 + HCO_3^- + NH_4^+ + H_2O \longrightarrow C_5H_7NO_2 + 5\ O_2$$

On the basis of the results of both laboratory studies and theoretical calculations, the following overall reaction has been proposed to describe the autotrophic conversion of ammonium ion to nitrate (3):

Overall Reaction:

$$22NH_4^+ + 37O_2 + 4CO_2 + HCO_3 \longrightarrow C_5H_7NO_2 + 21NO_3^- + 20H_2O + 42H^+$$

Nitrification will occur in most aerobic biological treatment processes when the operating and environmental conditions are suitable. Factors that affect nitrification in all systems include 1) liquid temperature, 2) pH, 3) presence of inhibitors, and 4) presence of carbonaceous matter in the wastewater. Other factors that influence the degree of nitrification obtainable in a trickling filter include process variables such as depth of filter, size and type of medium, and organic loading.

CHAPTER II

LITERATURE REVIEW

A. Trickling Filter Characteristics

In order to understand the nitrification process in a trickling filter, it is important to first understand some overall aspects of the process itself.

Trickling filters have been utilized in the United States for the biological treatment of wastewater for about 85 years. Actually, the process does not employ filtration; instead, the wastewater is trickled over a medium with microorganisms growing on the fixed surfaces. These bacteria utilize the dissolved nutrients in the wastewater for food, thus creating a purification effect. Void spaces within the medium permit the ventilation of air so that the oxygen required for growth may be transferred across the bacterial slime layer. As the microorganisms grow and the slime layer increases in thickness, the supply of diffused oxygen is consumed before it can penetrate the full depth of the layer. Thus, an anaerobic environment is established near the surfact of the medium.

As the slime layer increases in thickness, the adsorbed food material is metabolized before it can reach the microorganisms near the medium face. As a result of having no external food source available, the microorganisms near the medium face enter into an endogenous phase. In this phase, the microorganisms lose their ability to cling to the

medium surface. The trickling fluid then shears the slime layer off the medium, and a new slime layer will start to grow. The phenomenon of losing the slime layer is called "sloughing." It is primarily a function of the food and hydraulic loading on the filter. The hydraulic loading accounts for shear velocities, and the food loadings (in weight per unit time) accounts for the rate of metabolism in the slime layer. Food is herein defined as the energy-yielding substance, i.e., organic carbon for heterotrophic bacteria and NH_3 and NO_2 for nitrifying bacteria.

Trickling filters are classified by hydraulic and food loadings as high-rate or low-rate (sometimes called standard-rate). The low-rate filters generally accomplish nitrification, while high-rate filters do not. Other factors are shown in Table I.

TABLE I

A COMPARISON OF LOW-RATE AND HIGH-RATE TRICKLING FILTERS

Factor	Low Rate	High Rate
Hydraulic Loading		
MGAD	1 to 4	10 to 40
gal/ft^2/day	45 to 140	500 to 2000
Organic Loading		
lb BOD_5/acre-ft-day	300 to 1000	1000 to 5000
lb BOD_5/1000 ft^3/day	2 to 14	50 to 300
Mean Cell Residence Time (Θ_c)	high	low
Amounts of Sludge Produced	low	high
Removal of Inorganic Nutrients by Synthesis	low	high
Reaction to Shock Loading	reasonable stability	less stability

Various types of medium have been utilized in trickling filters or biological towers. Broken stone has been the traditional medium; however, gravel, slag, wooden slats, and plastic media have also been used. Redwood slats and polyvinyl chloride (PVC) media are the most popular types being installed today. These types have a high void space per volume ratio, which provides excellent ventilation and prevents clogging. The four leading plastic media in use are sold under the trade names of Flocor, Surfpac, Cloisonyle, and Vinyl Core. These have specific surface areas of 27, 56, 66, and 30 ft^2/ft^2, respectively, with corresponding void ratios of 97, 94, 94, and 96 percent.

B. Previous Investigations

A great deal of research effort has been exerted in order to define the operational and environmental effects upon nitrification in a trickling filter. Some earlier studies revealed that carbonaceous oxidation and nitrification can occur simultaneously in trickling filters at different levels. Jenkins (5) found in his studies on biological oxidation of carbohydrates that "in the lower sections, where organic matter is present in low concentrations (0.01 to 0.05% sucrose), the filter is specialised for nitrification." It was also shown, however, that complete absence of carbohydrate is not essential before nitrification can occur.

In 1948, Heukelekian (6) conducted a series of trickling filter exeperiments with domestic sewage. He used a high-rate rock filter loaded at 2250 lbs BOD/acre-ft/day and a low-rate rock filter loaded at 600 lbs BOD/acre-ft/day. Based upon cultivation techniques, he found that both classifications of filters contained nitrifying flora.

However, the high-rate filter produced an average of 0.7 ppm NO_3-N after three feet of depth, while the low-rate filter produced an average of 8.4 ppm NO_3-N after 6½ feet of depth. Based upon the high-rate filter loadings, he found that the lower the rate of application, the greater the nitrate production until the rate of application approached those in the standard filter.

The team of Grantham, Phelps, Callaway and Emerson (7) conducted a group of trickling filter studies. They used native Florida materials as media for the treatment of domestic sewage. The authors found with each type of medium that as the BOD_5 concentration decreased with depth, the nitrification increased with depth after a definite lag period. One of their conclusions was that nitrification in a trickling filter follows the monomolecular reaction pattern and depends to some extent upon the type of filter medium and BOD_5 loading rates employed. With lower BOD_5 loading rates, it was shown that nitrification is more rapid and more complete. The authors formulated a mathematical equation which states that the nitrogen oxidation rate per interval of depth in a filter bed is proportional to the concentration of remaining oxidizable nitrogen. Other variables that influence nitrification, such as temperature and pH, were not included in their equation.

Sorrels and Zeller (8) conducted research upon four pairs of filters--one primary (6 ft deep) in series with a secondary (2 ft deep), while using domestic wastewater. They report that in the primary filters, the removal of NH_3-N accompanied BOD removal with only a small formation of oxidized nitrogen.

In the secondary filters, there was a considerably higher reduction in ammonia-nitrogen comparable to an equivalent production of oxidized

nitrogen. Both of these two characteristics decreased as the carbonaceous loadings increased. The authors report the primary filter functioned largely by assimilation and synthesis, while the secondary filter functioned by oxidation.

Another fixed-bed experiment was conducted in 1969 by Balakrishnan and Eckenfelder (9), using a medium of 1-in. raschig rings and 1-in. beryl saddles in a 6-ft deep tower. The waste source came from the final clarifier of a contact stabilization activated sludge plant. They found that the percent nitrification increased from 52 to 72 percent when the hydraulic loading decreased from 30 to 10 MGAD. A higher percent nitrification could be obtained by increasing the depth or by decreasing the hydraulic loading. The authors also report that there appears to be a very good correlation between the specific surface of the medium and the nitrification rate constant. The characteristic curves from the experiment for a temperature range of 15^{o}-30^{o}C showed that the temperature has a great deal of influence upon nitrification. The authors developed an equation for percent nitrification in a trickling filter:

$$\text{percent nitrification} = 1 - S/S_o = 1 \exp\left[-KD/Q^n\right]$$

where

S_o = influent NH_3-N concentration

S = effluent NH_3-N concentration

K = reaction constant related to specific surface of media

D = depth

Q = hydraulic loading rate

n = constant related to the specific surface and the configuration of packing

However, the effects of temperature, pH, inhibitors, and carbonaceous matter was omitted from the equation.

An extensive pilot plant study upon nitrification in an oxidation tower was reported in 1973 by Duddles, Richardson, and Barth (10). This investigation used a 21.5-ft x 36-in diameter pilot plant with Surfpac plastic medium. The tower was used to treat the unchlorinated final effluent from a municipal rock trickling filter plant. (The organic and hydraulic loadings on the rock filters were great enough so that nitrification did not occur.) The influent to the pilot plant was fed at controlled hydraulic rates with a BOD_5 concentration below 20 mg/l for a loading less than 15 lb BOD_5/1000 ft^3/day. Total organic carbon (TOC) levels in the influent averaged 26 mg/l, while NH_3-N concentrations ranged from 10 to 20 mg/l. A high percentage of nitrification (80-90%) was recorded, whereas the average TOC removal was 6 mg/l.

According to the authors, there was a definite relationship between the increase in hydraulic loading and the decrease in nitrification performance. They found that effective (greater than 80%) nitrification is not feasible at influent flow rates greater than 10 gpm/ft^2. Recycling the tower effluent did not significantly improve the overall nitrification performance of the system. Temperature effects upon NH_3-N removal were quite pronounced. At 56°F, there was an 86% removal of NH_3-N, while only 61% removal was achieved at 46°F while maintaining a flow rate of 1 gpm/ft^2. It was also reported that the NH_3- N concentration in the final effluent was not reduced below a range of 1-2 mg/l. There was no mention of pH effect during the investigation.

Stenquist, Parker, and Dosh (11) reported an investigation using raw municipal and cannery wastes combined. This investigation studied

conditions necessary for nitrification in a combined carbon removal/ nitrification system. They found that under this regime, nitrification is principally dependent on the organic loading and temperature. The authors estimate that for significant nitrification to take place in the 21.5 ft tower, an organic loading less than 25 lb BOD_5/1000 ft/day is required.

Stover (12) conducted a nitrification study with an 8-ft deep x 1 ft x 1 ft biological tower using Flocor plastic medium. A synthetic carbohydrate waste was used with a COD:NH_3-N ratio of 20:1. Under closely controlled conditions, he applied various influent organic loadings from 88 to 313 lb COD/1000 ft^3/day. Nitrification did not occur at any of these loadings. Then a loading of 55 lb COD/1000 ft^3/ day was applied at an influent COD equal to 53 mg/l. After trickling over four feet of medium, the COD concentration in the waste stream had been reduced to 23 mg/l and remained at this same concentration throughout the rest of the tower. Then at the fifth foot, nitrification began and continued throughout the remainder of the tower as determined by increased NO_3-N production. The remaining ammonia-nitrogen was completely removed by nitrification before the eighth foot had been reached.

Stover based his results upon an approach suggested by Kincannon and Sherrard (13) and used previously by Bentley (14). The performance of the tower was examined in terms of mean cell residence time (Θ_c) and food-to-microorganism ratio (F/M). As described by Bentley, the mean cell residence time corresponding to an organic loading of 55 lbs COD/ 100 ft^3/day was approximately five days. Stover believed the reason the filter would not nitrify earlier was that the organic loadings were too high and thus the mean cell residence times were too low. Since

the biological filter did not employ recirculation of biological solids, the controlling factor, instead, became the amount of biological solids wasted from the system. Therefore, in order to increase the mean cell residence time high enough to achieve nitrification, he found it necessary to decrease the total organic loading applied. When the mean cell residence time was increased to five days, complete nitrification was attained.

During his experiment, all but the "residual" COD had been removed before nitrification began in the fifth foot. That is, the COD had been removed to its lowest level and no further significant growth of heterotrophic carbonaceous organisms occurred during nitrification.

Stover discussed possible explanations for nitrification to occur at lower depths than carbonaceous growth. One explanation is a competition type relationship between heterotrophic and autotrophic microorganisms. The heterotrophic microorganisms are capable of faster growth rates (μ), and are not as sensitive to environmental changes as are nitrifiers, whereby they would be capable of a crowding-out type of effect upon the nitrifiers. According to him, it is possible that the production of compounds toxic to nitrifying microorganisms is made by heterotrophic microorganisms. This theorem was partially verified by a fluidized batch study conducted by the same author. Within this experiment, he added an organic carbon source (glucose) to a nitrifying activated sludge system. No inhibition was found up to a concentration of 750 mg/l COD. However, upon the addition of heterotrophic microorganisms with the glucose under a controlled experiment, distinct inhibition resulted.

Saidi (15) presented a similar occurrence with an extended

aeration activated sludge investigation. He reported that when the organic loadings to the system were suddenly increased, the reactor biological solids immediately increased. Then the dominant form of effluent nitrogen changed from nitrate-nitrogen to ammonia-nitrogen.

Murthy (16) showed a similar phenomenon when he gradually increased the substrate concentration over an 8-day period in a nitrifying system. During this time, the reactor solids and effluent NH_3-N increased, and NO_3-N decreased. Thus, nitrification was inhibited by an increase in heterotrophic growth.

Yang (17) also reported varying reactor solids concentration accompanied by varying degrees of nitrification in a long-term extended aeration total recycle investigation.

The purpose of this study was to continue the research upon carbonaceous inhibition of nitrification in a biological tower that was initiated by Stover. It would be very useful to determine if there is a certain organic carbon concentration after heterotrophic growth at which nitrification will commence in a biological tower process. The design engineer could use the information in order to determine the required level of secondary treatment required, so that proper design for ammonia oxidation could result. It would also be quite helpful to the operating engineer to learn what effect upon the nitrifying portion could result by a leakage of carbonaceous matter from the carbonaceous portion.

CHAPTER III

MATERIALS AND METHODS

A. Experimental Approach

In order to determine the COD concentration at which nitrification will commence in a biological tower, an experimental pilot plant reactor was utilized. A synthetic waste feed of completely soluble carbohydrate substrate was passed over the 9-ft deep tower at a constant flow rate of 1000 gpd/ft^2. All experiments were conducted under closely controlled conditions. The only variation applied to the system was the influent feed concentration. This variation was made in order to change various depths at which nitrification would commence in the tower, if at all. The COD and carbonaceous BOD tests were used to measure the carbon concentration at various depths, while NH_3-N and NO_3-N were used to determine the nitrogen concentrations. A significant increase in the nitrate-nitrogen concentration at any depth of the tower was used to determine the occurrence of nitrification.

B. Experimental Apparatus

The biological tower utilized was in two parts, with the first section four feet deep and the second section five feet deep. Each section contained one cubic foot (1 ft x 1 ft x 1 ft) modules of Flocor plastic medium as the contact bed. After each module, there was a

4-inch void space in order to permit sampling of the wastewater flowing through the system. A diagram of the system is shown by Figure 1.

The Flocor plastic medium used during the study was originally developed by the Imperial Chemical Industries, Ltd., London, England, and was previously manufactured in the United States by the Ethyl Corporation. This particular medium is made of polyvinyl chloride with 2¼-inch triangular openings to yield a surface area of 27 ft^2 per cubic foot. Thus, the 97% void space provided by the medium affords excellent ventilation upon the fixed surfaces for microbial metabolism.

The hydraulic flow rate applied to the system was controlled by means of a constantly overflowing tank supplied with potable water from the Stillwater (Oklahoma) distribution system. A rotameter regulated the flow fed to the primary wet well from the constant head tank. Within this well, the city water was mixed with a flow of concentrated synthetic waste by means of a Sargent magnetic stirrer.

The synthetic waste feed used sucrose as the carbon source and growth-limiting nutrient, as shown by Table II.

The COD:NH_3-N ratio of 10:1 as supplied by the ammonium sulfate was in excess of the requirements for synthesis by heterotrophic microorganisms. The excess NH_3-N was used to supply metabolism requirements for any nitrifying microorganisms.

During feed preparation, 40 ml of 16 N sulfuric acid was added to assist the dissolution of the concentrated waste constituents and to prevent biological growth in the feed bottle and lines. Therefore, the concentrated feed possessed a low pH, but after mixing with large quantities of tap water, the flow entering the tower possessed a pH value between 7.2 and 7.5--well within the range for microbial growth to

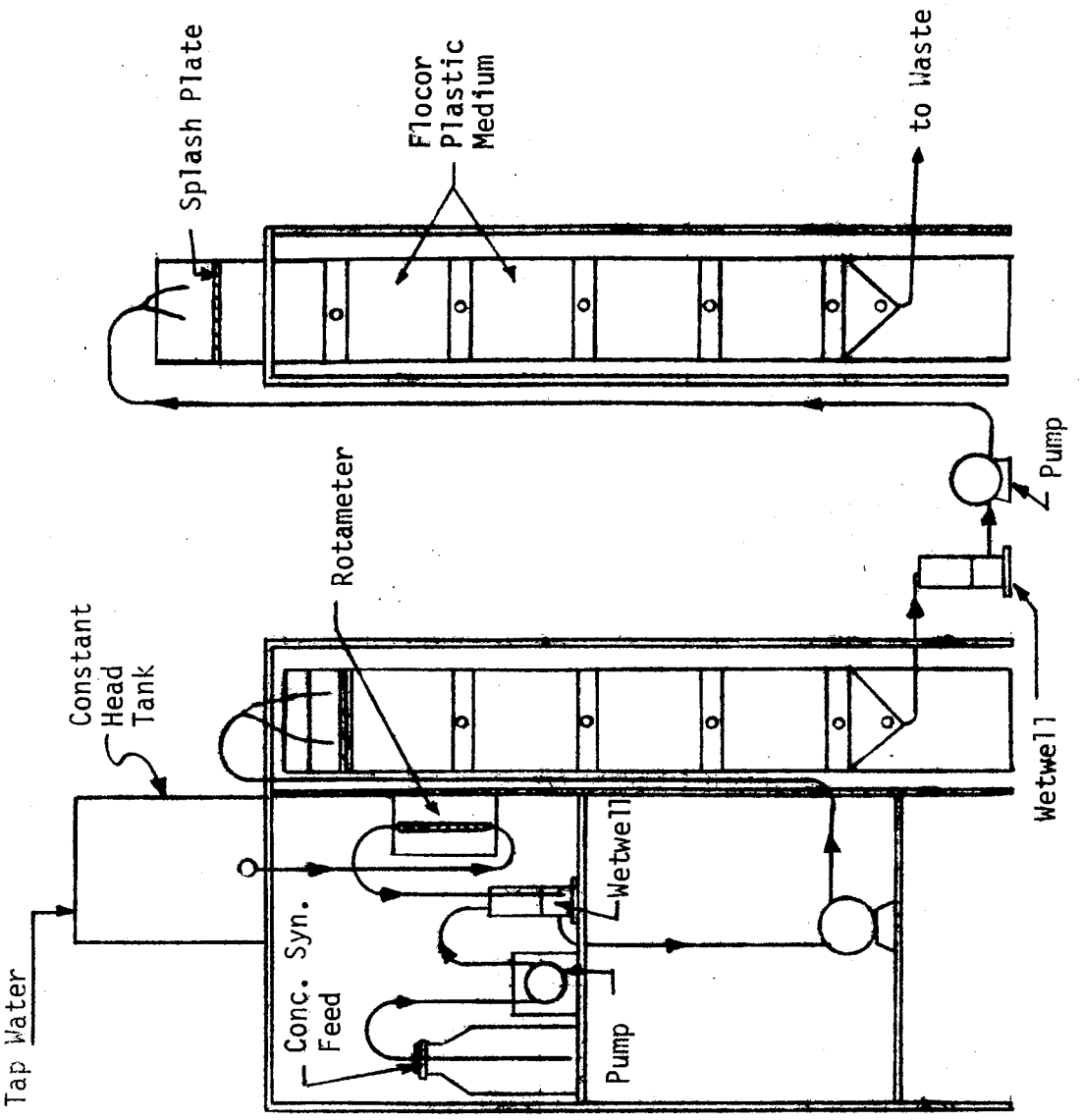

Figure 1. Experimental Fixed-Bed Reactor

occur. The concentrated feed was prepared in a 40-liter Pyrex bottle and was stirred slowly and continuously to ensure a constantly homogenous solution. The concentrated feed was pumped to the primary wet well by a variable speed Cole-Parmer Master-flex tubing pump (Model WZ1R031). Desired feed concentrations could then be obtained by varying the amounts of waste pumped to the wet well. After mixing, the flow was conveyed from the wet well to the head of the tower's first section by means of a Teel Rotary-Screw pump (Model I P610). The pump was driven by a Dayton single speed motor (Model KS55JXBJB-913).

TABLE II

COMPOSITION OF THE SYNTHETIC WASTE FOR 100 mg/l SUCROSE AS THE GROWTH-LIMITING NUTRIENT

Constituent	Concentration
$C_{12}H_{22}O_{11}$ (sucrose)	100 mg/l
$(NH_4)_2SO$	50 mg/l
$MgSO_4 \cdot 7H_2O$	10 mg/l
K_2HPO_4	6 mg/l
$MnSO_4 \cdot H_2O$	1 mg/l
$CaCl_2$	0.75 mg/l
$FeCl_3 \cdot 6H_2O$	0.05 mg/l

The distribution of the synthetic wastewater across the 1.0 ft^2

of horizontal surface area of the reactor was achieved by the use of a plastic Y in the feedline connected to two 6-inch lengths of tubing. The split waste stream was further distributed by a Plexiglass splash-plate with staggered rows of 3/16-in diameter holes at 1½ inches on center each way.

After flowing through the first section of the tower, the wastewater was collected into a trough and channelled into an intermediate wet well. The flow was then pumped over the tower's second section by mechanisms identical to the first section. Final effluent from the tower was discharged into the local sanitary sewer. The temperature of the wastewater throughout the experiment ranged from 22°C to 26°C. The small range of pH values (7.2 to 7.5) was due to the high quality of the tap water supply. The effect of changing temperature and/or pH during the experiment was considered negligible compared to the precision of the analytical determinations.

C. Experimental and Analytical Procedures

The reactor was seeded with microorganisms from an activated sludge pilot plant located in the bioenvironmental engineering laboratories of the Oklahoma State University. The original seeding of the activated sludge unit was accomplished with settled sewage from the primary clarifier of the Stillwater (Oklahoma) pollution control plant.

Throughout the entire investigation, a constant hydraulic flow rate of 1000 gal/day/ft^2 was applied to the system. The tower was placed in operation during May, 1974, at an initial COD concentration of 70 mg/l. During the next several weeks of operation, the microbial population began to acclimate to the wastewater, and gradually reached

steady state conditions as determined by periodic determinations. During this period, the researcher improved his techniques for operation, sampling, and analytical determinations required for the investigation. The initial experiment run was conducted during the dates of July 11, 12, 14, and 31, 1974. Another one-foot module of medium was added at the 6-ft level on July 19, and the growth was allowed to acclimate before the July 31 testing date. The feed concentration was changed, and a new run was initiated. Each run consisted of a minimum 4-day equilibration period, followed by a minimum of three consecutive or nearly consecutive days of sampling at each one foot depth of the tower. Steady state conditions were ascertained by obtaining nearly identical values of COD, NO_3-N, and NH_3-N over a three-day period. (BOD analyses were conducted on a less regular basis.) Results of analyses obtained over the three-day period were averaged and recorded as the values for that particular parameter for that particular run.

Samples for the various analyses were taken at each foot of depth, using a modified plastic pipe which had the upper half of its wall removed to form a trough-like sampler. The sampler was inserted into the void space and moved back and forth horizontally across the flow so that a composite sample was obtained at each foot of depth. The samples were collected into 250-ml Erlenmeyer flasks for further handling. COD, NH_3-N, and NO_3-N analyses were made upon wastewater filtered through HA 0.45 μ Millipore filter paper. The 0.45 μ filter removed all suspended solids material in the waste fluid so that the determinations were made upon soluble material only. Filtrate COD determinations were made in duplicate, according to Standard Methods (18), utilizing a 20-ml sample size.

The ammonia-nitrogen analyses were made using a method developed by Niss and described by Ecker and Lockhart (19). Two reagents were employed. Reagent A contained 9.79 grams sodium citrate, 3.54 grams citric acid, 20.00 grams phenol, and distilled water to one liter. Reagent B contained 15.0 grams boric acid (H_3BO_3), 20.0 grams sodium hydroxide, 75.0 ml of commercial Chlorox bleach, and distilled water to 500 ml. The cell-free samples were diluted if needed to give between two and 20 mg/l of NH_3-N. To 1.0 ml samples were added 5.0 ml of Reagent A and 2.0 ml of Reagent B. The samples were mixed, heated in a boiling bath for five minutes, and cooled rapidly in ice water. The optical density for the sample was determined at a wavelength of 615 millimicrons against a distilled water-reagent blank using a Bausch and Lomb 120 Spectrophotometer. The optical density readings were compared to a standard curve with known concentrations of NH_3-N.

Nitrate-nitrogen was determined by the Brucine method outlined in Standard Methods (18). The optical density for the samples was determined by identical methods as ammonia-nitrogen, except at a wavelength of 410 millimicrons.

BOD analyses were determined according to Standard Methods (18), while using the Winkler method for determination of dissolved oxygen. Sample dilutions were made according to Sawyer and McCarty (20). Nitrification was eliminated in the BOD determinations by a method described by Siddigi, Speece, Engelbrecht, and Schmidt (21). Ten ml of a 3M NH_4Cl were placed in the 300-ml bottles to yield a 0.10 M NH_4Cl concentration when the bottle was full. According to the authors, the nitrification is suppressed in the 5-day determination, and only carbonaceous BOD is measured.

CHAPTER IV

RESULTS

The results of this investigation are presented by graphical relationships of the four analytical parameters utilized vs depth. Results from the four steady state runs with influent COD concentrations of 68, 74, 53, and 44 mg/l are shown first. A composite of these data along with plots of COD vs NH_3-N removed and COD vs NO_3-N produced are also presented. Then the results from immediate organic shock loads with influent CODs greater than 80 and 150 mg/l are shown by similar graphical representation. The influent COD:NH_3-N ratio remained at 10:1 throughout the investigation, with a constant flow rate of 1000 gal/day/ft^2. Any significant increase in nitrate-nitrogen concentration was used to indicate nitrification within the tower.

A. Steady State Conditions

The COD removal, NH_3-N removal, and NO_3-N production for a wastewater containing 68 mg/l COD are shown in Figure 2. The best straight line fit for these data was found with arithmetic plots. Therefore, the change in concentration per depth was equal to a constant, i.e., $\frac{dC}{dD} = k$. This equation implies that within the reactor, changes in concentration followed zero order kinetics.

The removal was in two phases, which reflects a change of growth kinetics within the reactor. The first phase had a removal rate of

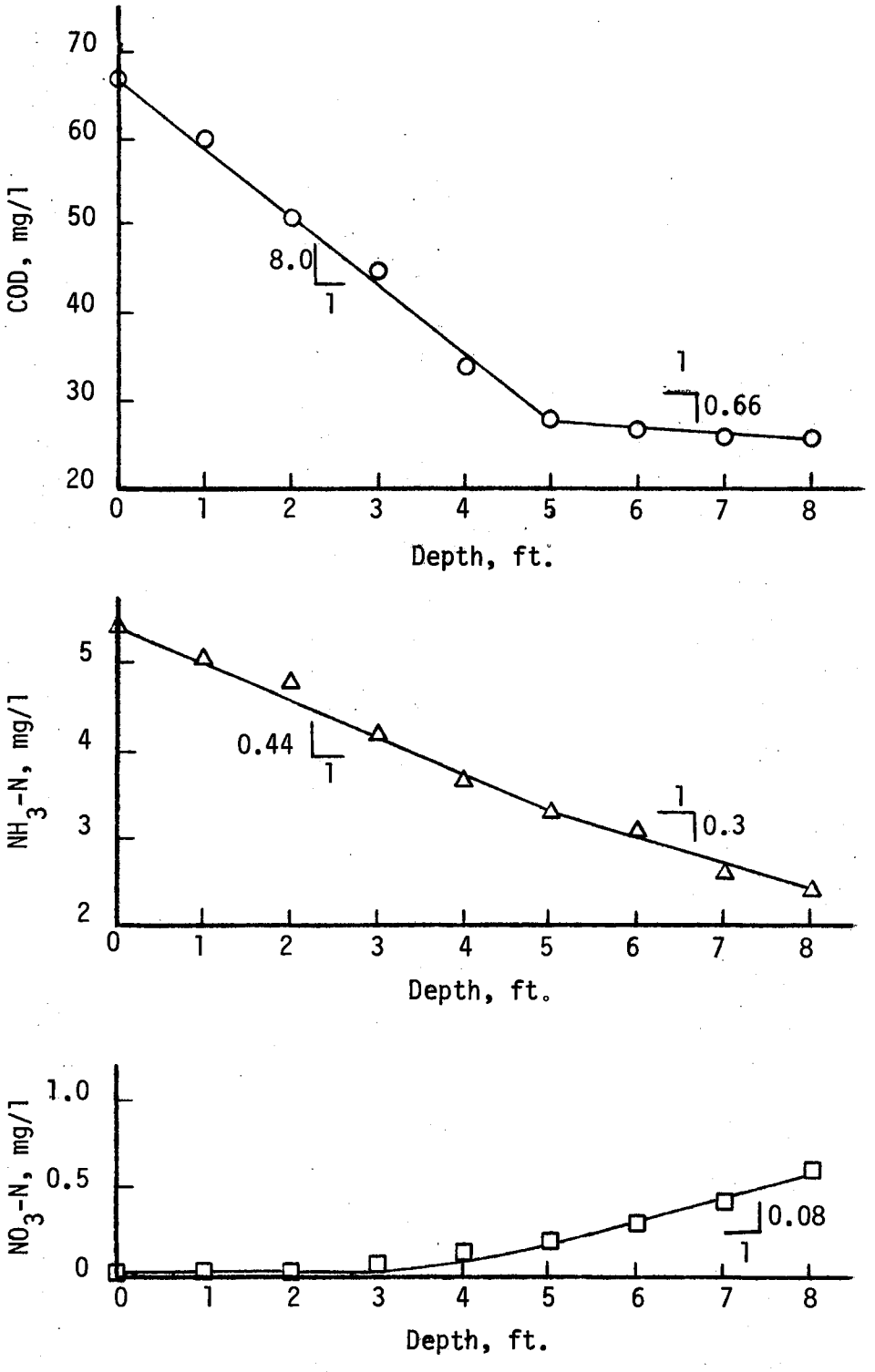

Figure 2. Parameters vs Depth, July 11, 12, 14, and 31, 1974. COD_i = 68 mg/l

8.0 mg/l/ft for the first five feet, and a second removal rate of 0.66 mg/l/ft for the last three feet.

The NH_3-N removal also exhibits zero order kinetics with a removal rate through the first five feet equal to 0.44 mg/l/ft. Then the rate changes and the concentration continues to decrease at a rate of 0.3 $mg/l/ft^2$ throughout the remaining depth of the tower. Both the COD and NH_3-N removals changed rates at the same depth of five feet.

There was no increase in NO_3-N concentration during the first three feet. Then, after two feet of increasing formation rate, there was zero order kinetics at a rate of 0.08 mg/l/ft for the last three feet of depth.

By dividing the initial COD rate by the Initial NH_3-N rate, we find a ratio of 18.18. This ratio is near the value of 20:1 that occurs during heterotrophic growth. One may reason that heterotrophic growth occurred during the first five feet of depth while nitrification was at a very low rate. Then, during the second phase, a COD:NH_3-N removal rate ratio of 2.2 was found. At this low ratio, the increasing rate for nitrification followed zero order kinetics.

During the second run of August 7, 8, and 9, the influent COD concentration was increased to 74 mg/l. Results from this run are shown by Figure 3. Again, the COD removal was in two phases with a change in kinetics occurring during the fifth foot. Phase I occurred over the first four feet, with a removal rate identical with the first run--8.0 mg/l/ft. But Phase II had a much larger rate for the last three feet than did the first--1.75 mg/l/ft. The carbonaceous BOD_5 results from August 7 are also shown with a concentration equal to 15 mg/l after the fifth foot, decreasing thereafter at a rate of 0.5 mg/l/ft.

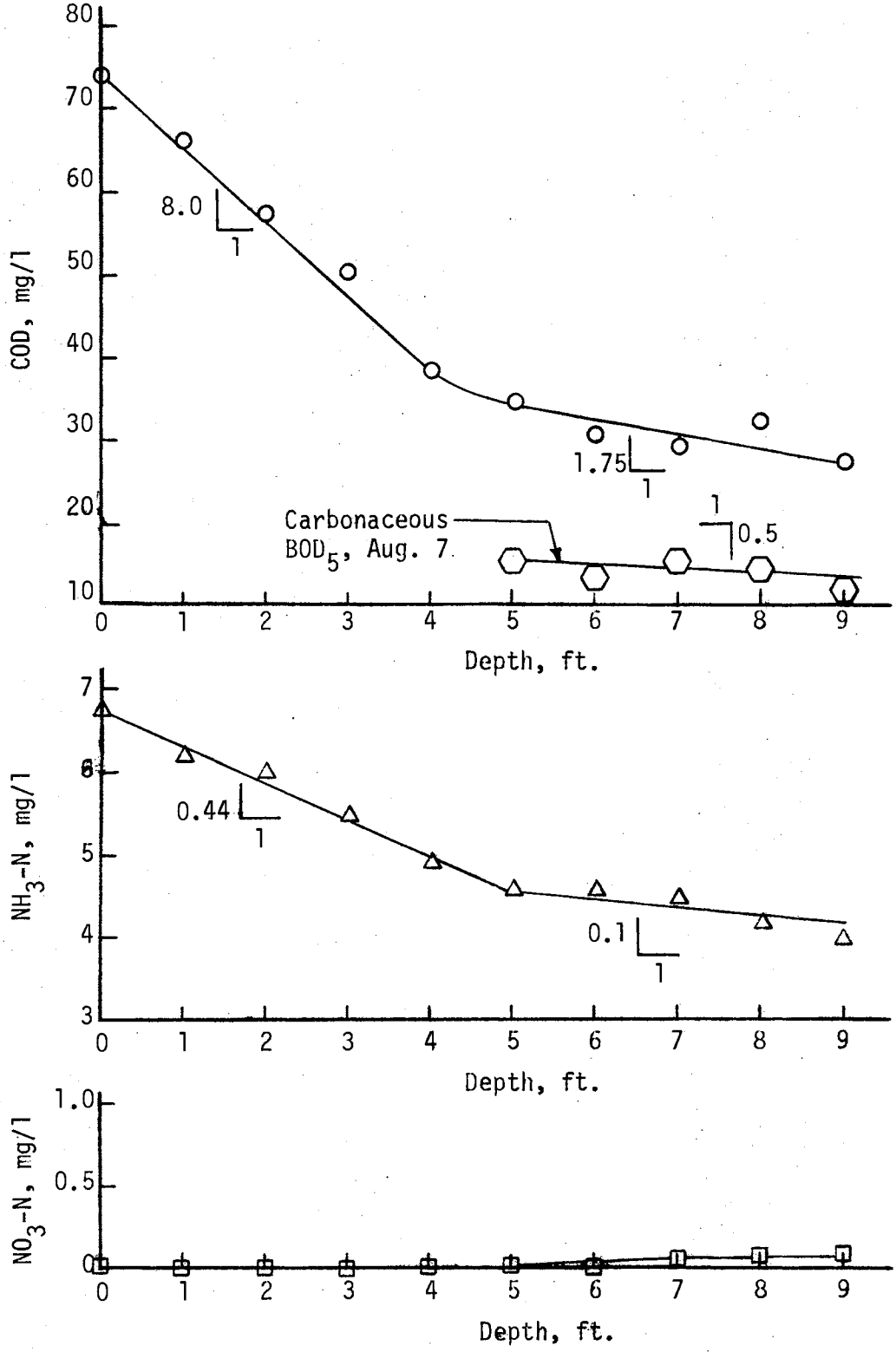

Figure 3. Parameters vs Depth, August 7, 8, and 9, 1974.
COD_i = 74 mg/l

Ammonia-nitrogen removal exhibits a change in rate at the 5-ft depth that corresponds to the depth at which the COD removal rate changed. Again, Phase I exhibited a removal rate identical with the first run--0.44 mg/l/ft. However, Phase II over the last four feet showed a removal rate equal to 0.1 mg/l/ft.

The Phase I COD removal rate to NH_3-N removal rate equalled 18.18 --exactly as did the first run. Corresponding to this indicator of heterotrophic growth, there was no nitrification over the first five feet. But during Phase II, the removal ratio for COD to NH_3-N was 17.5, again an indicator of heterotrophic growth. The nitrification over this phase was very limited, with only 0.1 mg/l NO_3-N produced. Even though the COD and NH_3-N removal occurred in two phases, there was no significant nitrification during this run.

Results from the third run of August 14, 15, and 16, are shown by Figure 4. During this run, the influent feed was decreased to a COD concentration of 53 mg/l. During COD removal, a much lower initial rate of 6.4 mg/l/ft was recorded. Following a change in kinetics after the fifth foot, a much lower removal rate of 0.075 mg/l/ft was found for the last four feet.

Similar to COD removal, the NH_3-N removal exhibited two phases, with a rate change after the fifth foot. This time, the initial removal rate was much lower at 0.3 mg/l/ft. During Phase II, over the last four feet the rate was 0.18 mg/l/ft. Removal ratio for COD and NH_3-N over the first portion was 21.3, thus there was heterotrophic growth. As one might suspect, there was no nitrification during the first three feet of this portion, as shown by no increase in NO_3-N. Then, during the fourth and fifth feet, the nitrification began until zero order kinetics was

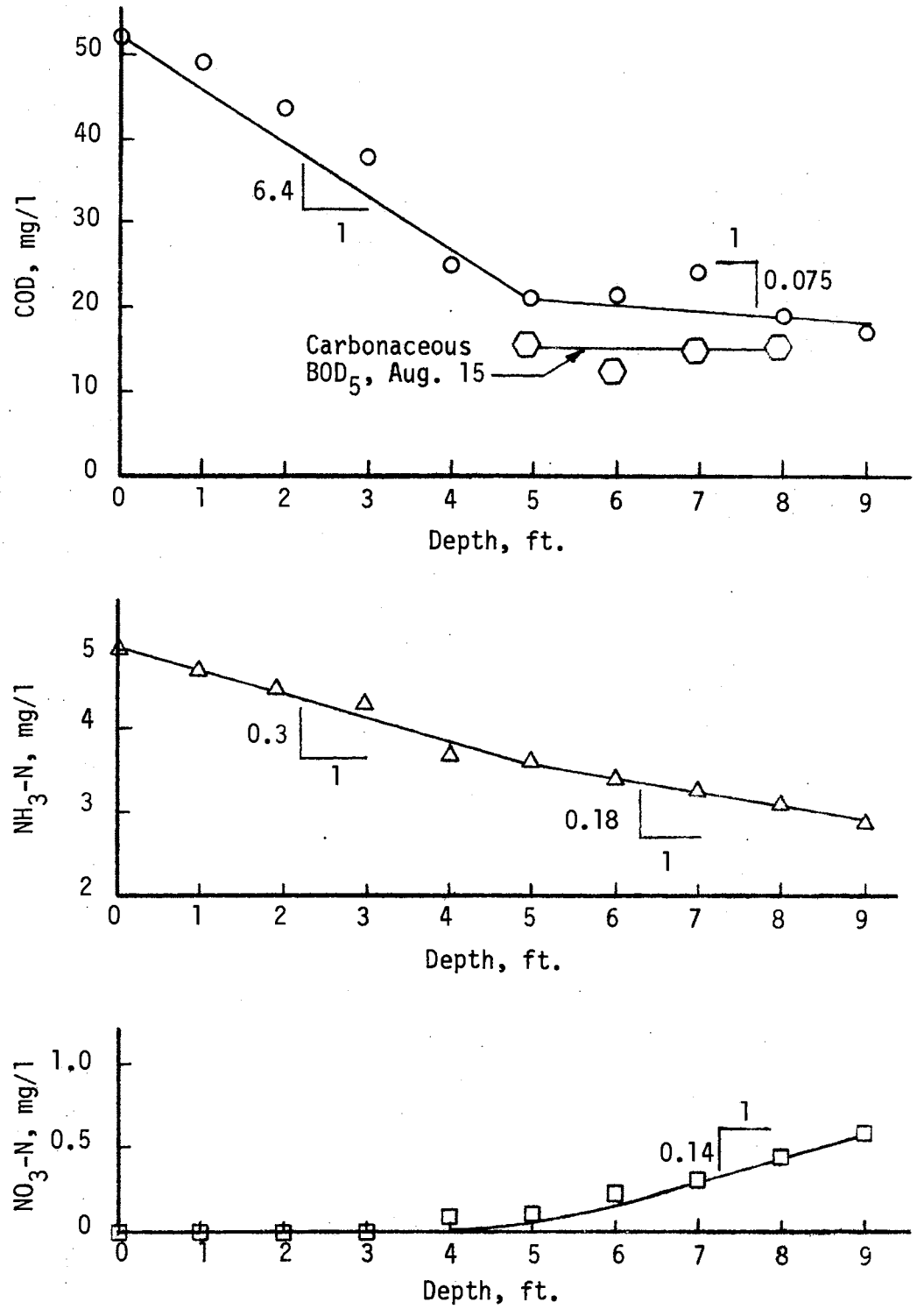

Figure 4. Parameters vs Depth, August 14, 15, and 16, 1974. COD_i = 53 mg/l

established over the last three feet of depth. The COD to NH_3-N removal rates for this section (Phase II) was 0.412. Therefore, with the signified low heterotrophic growth, a high nitrification rate of 0.14 mg/l/ft was recorded. This nitrification rate is even higher than the rate found in the first run at 0.08 mg/l/ft.

Another significant factor is the rate of carbonaceous BOD_5 removal over the last four feet of depth. During the second run, a rate of 0.05 mg/l/ft was found, corresponding to no significant nitrification. However, during this run, the carbonaceous BOD_5 concentration was constant (no decrease) and a high nitrification rate resulted.

Influent feed for the fourth steady state run of August 22, 23, and 24 (Figure 5) was reduced to a COD of 44 mg/l. A first phase COD removal rate similar to the third run was found at 6.5 mg/l/ft. Then the change in COD removal kinetics occurred at one foot less depth, i.e., the fourth foot. Thereafter, the COD concentration remained constant throughout the remainder of the tower at 18 mg/l.

At this same 4-ft depth, the NH_3-N removal also resulted in a change in kinetics. Also, like the COD removal rate, the NH_3-N removal rate resembled that from the previous run at 0.325 mg/l/ft. The second phase NH_3-N removal rate was identical to the previous run at 0.18 mg/l/ft.

There was no nitrification during the first two feet, as reflected by the COD to NH_3-N removal ratio of 20.0 (indicating heterotrophic growth) for the first four feet. During the third and fourth feet, nitrification began until zero order kinetics were shown for the remainder of the reactor. The 0.16 mg/l/ft NO_3-N production rate nearly matches the 0.18 mg/l/ft reduction rate in NH_3-N. Therefore,

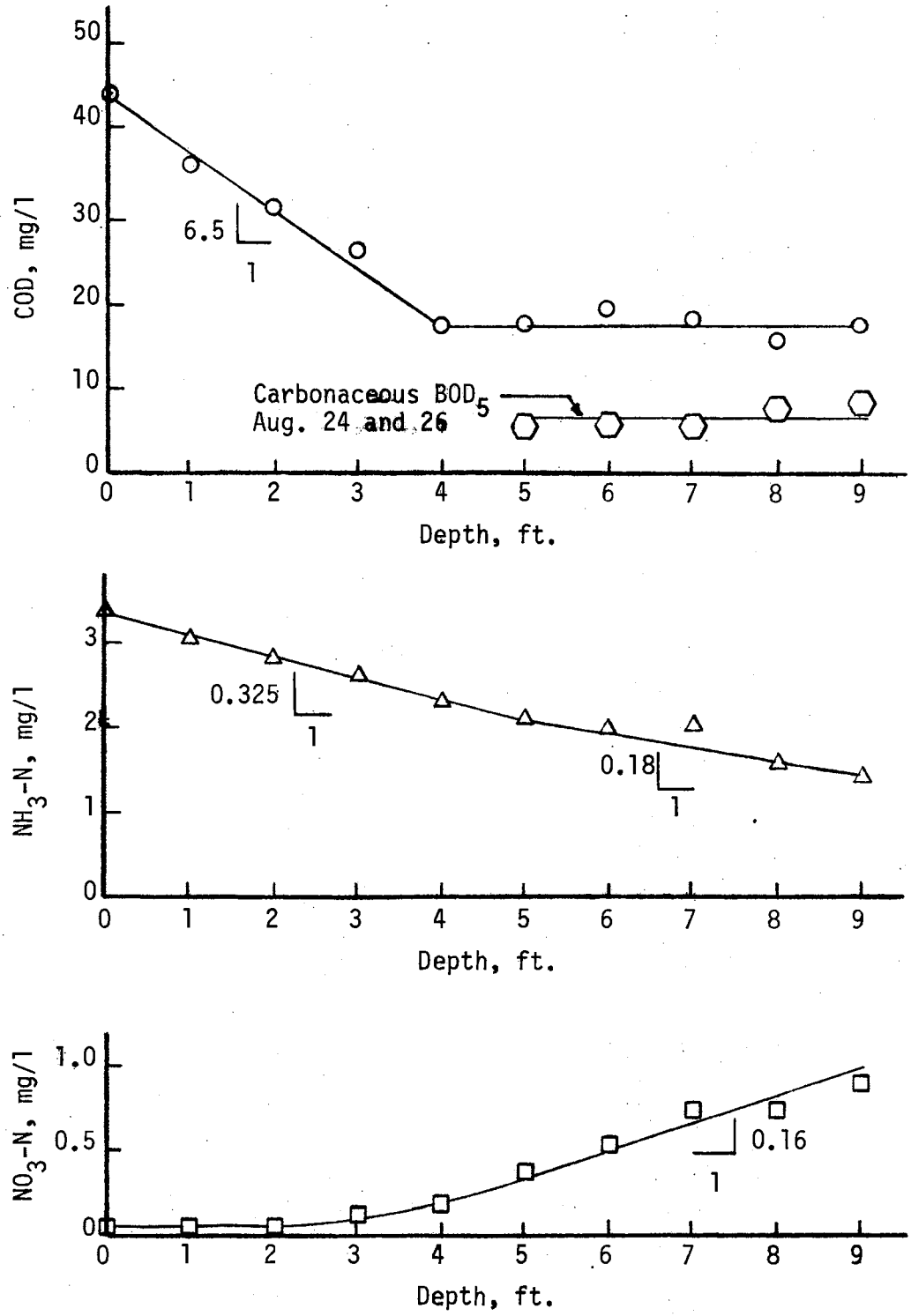

Figure 5. Parameters vs Depth, August 22, 23, and 24, 1974. COD_i = 44 mg/l

practically all of the NH_3-N was being nitrified into NO_3-N.

Again, the concentration of carbonaceous BOD_5 did not vary over the last four feet of depth. And again there was a high nitrification rate. The constant carbonaceous BOD_5 concentration for this run was 7 mg/l.

Figure 6 shows a composite of all steady state COD removal curves. It is noted that the removal of COD in all of the runs existed in two phases with definite changes in growth kinetics. By lowering the influent COD concentration, the second phase COD concentrations can also be lowered. Also, by sufficiently lowering the influent COD concentration, the change in growth kinetics can begin at an earlier depth in the tower. This was shown by the August 22-24 run with COD_i equal to 44 mg/l.

Figure 7 is a composite of the NH_3-N removals during the steady state runs. All of the curves exhibit two-phase removal, with changes in removal kinetics occurring at the same depth as the COD counterpart. In all cases, the removal rates during the second phase were lower than removal rates during the first phase.

The two uppermost curves in the figure have identical Phase I removal rates (0.44 mg/l/ft), while the two lower curves have very similar rates during this phase (0.3 and 0.325 mg/l/ft). The two curves in the center have similar influent NH_3-N concentrations (5.5 and 5.0 mg/l). Yet, the NH_3-N removal rates are quite different (0.44 to 0.3 mg/l/ft), since the initial COD concentrations varied by 15 mg/l. There is somewhat of a correlation between high influent COD concentrations and high NH_3-N removal rates during the first phase.

Figure 8 is a composite of the nitrification, i.e., NO_3-N

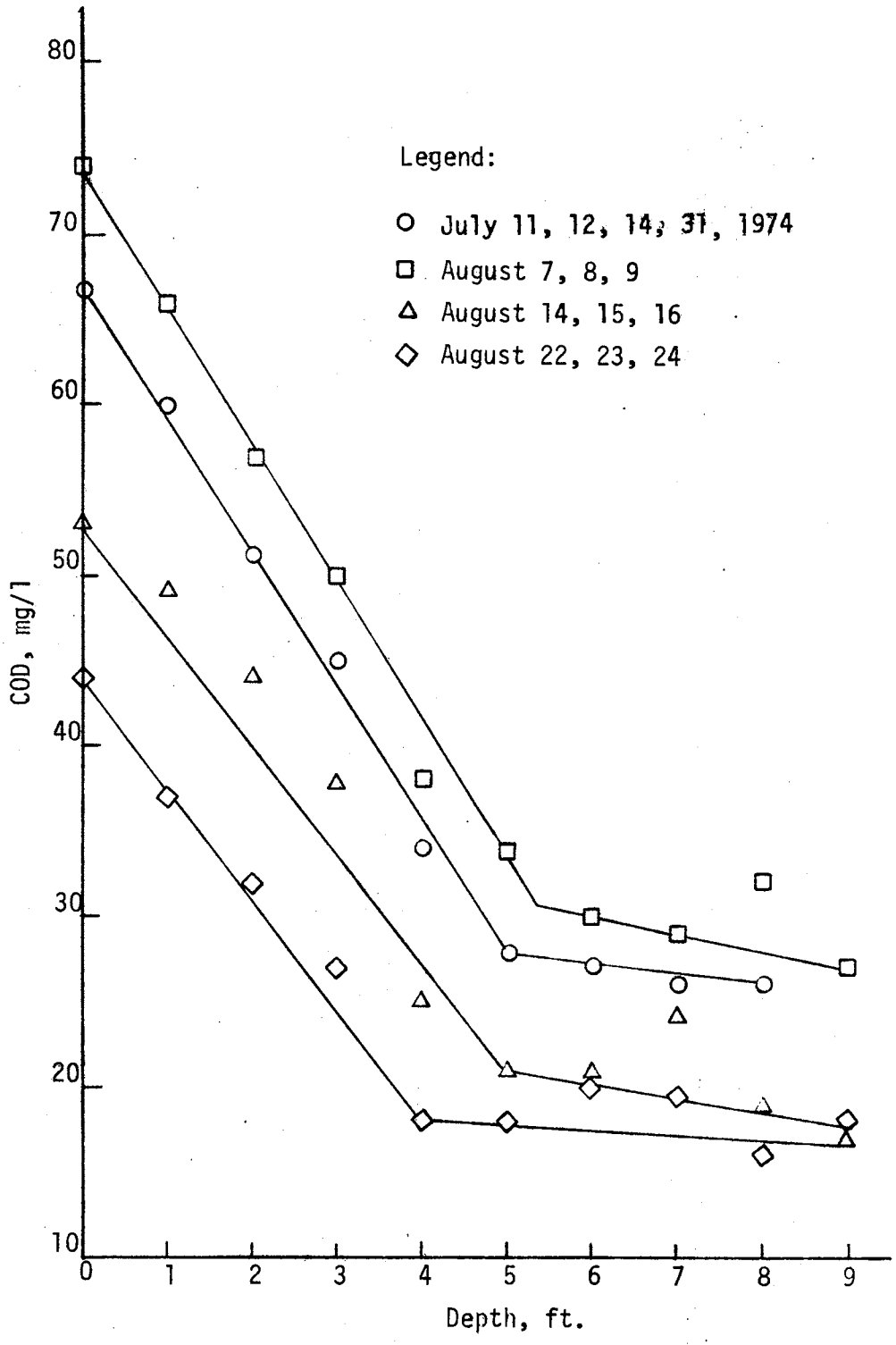

Figure 6. Composite COD vs Depth

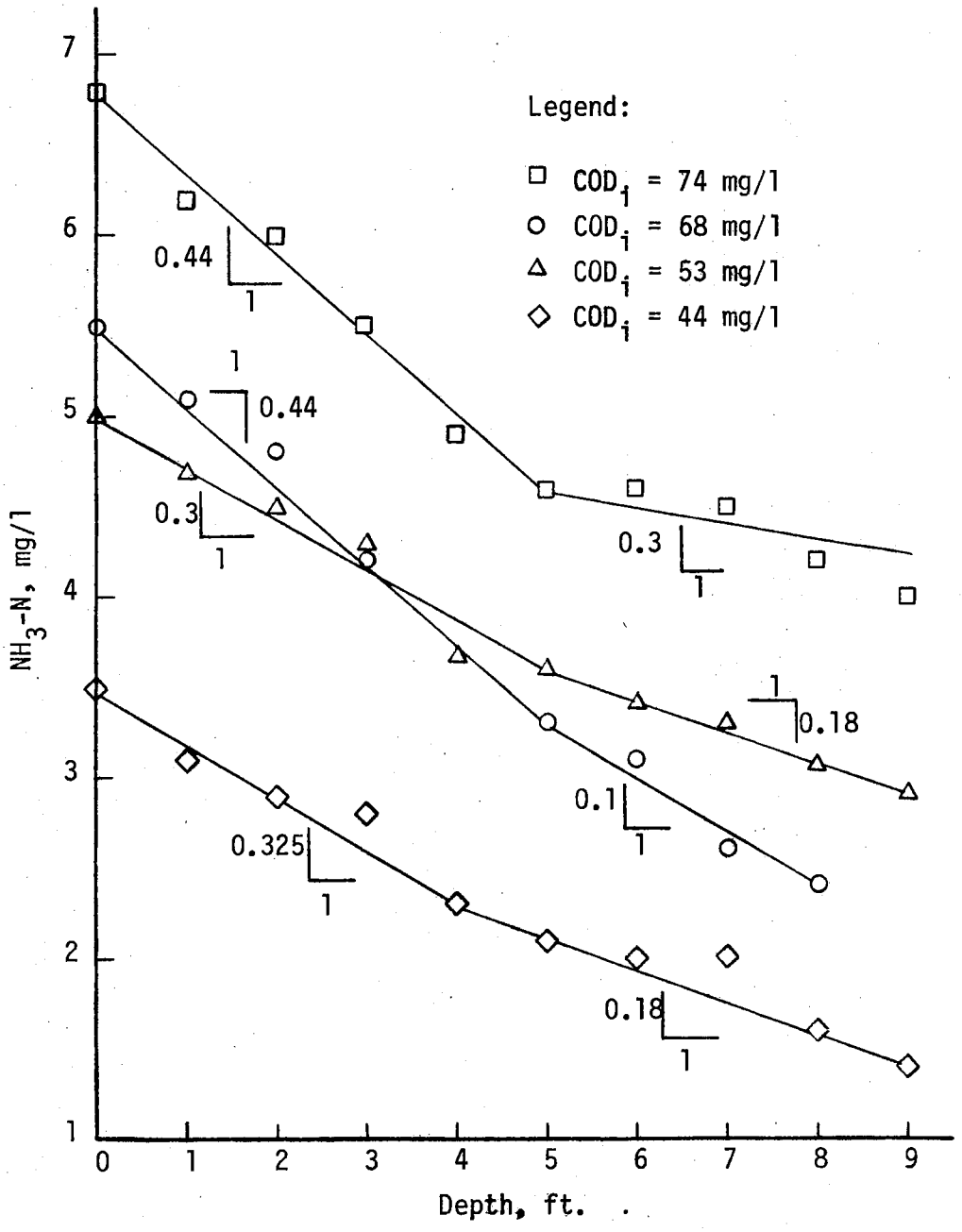

Figure 7. Composite NH_3-N vs Depth

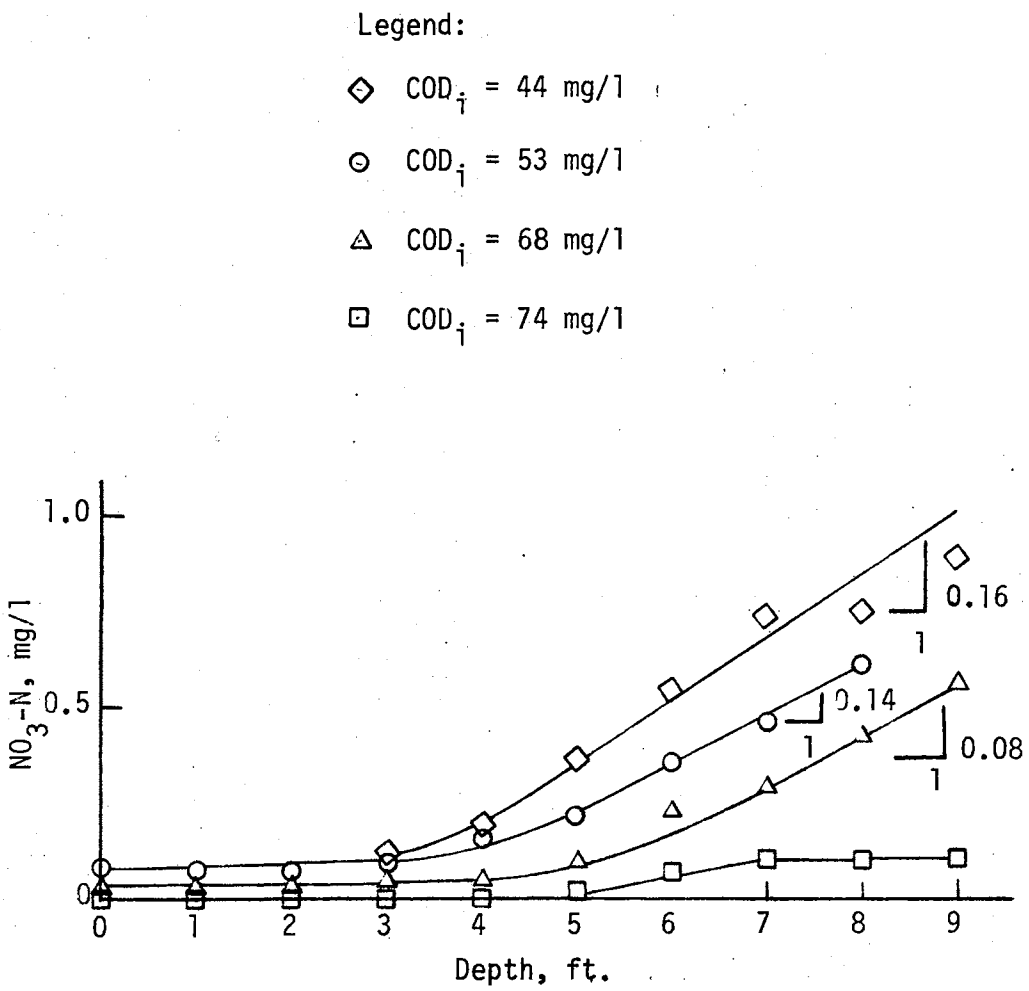

Figure 8. Composite NO_3-N vs Depth

formation during the steady state runs. All curves begin with definite lag periods, which are followed by transitions into zero order increasing rate kinetics except for the bottom curve with a COD_i = 74 mg/l in which nitrification ceases. In general, the lower the COD_i concentration, the higher the depth at which the transition begins. Also, the lower the COD_i concentration, the larger the nitrification rate and the greater the amounts of nitrate conversion.

A composite of COD concentration vs NH_3-N removed during the steady state runs is shown by Figure 9. The first portion of these curves corresponds to the first phase of both the COD and NH_3-N removals. Here the COD to NH_3-N removal ratios of 18, 18, 21, and 20 follow the classical 20:1 ratio associated with synthesis by heterotrophic growth. Then further down the curve, a change in ratio and kinetics takes place as heterotrophic growth begins to decrease. However, the NH_3-N continues to be removed by a second phase apparently not affected by the COD to NH_3-N ratio. The three curves with lower COD_i concentrations have more developed second phases than does the upper curve with a COD_i equal to 74 mg/l.

Figure 10 is a composite of the COD concentration vs nitrification, i.e., NO_3-N formation found in the tower during the steady state runs. These curves are in two stages (except the curve COD_i = 74 mg/l) which reflect two-stage kinetics within the biological tower. During the first stage, there is a rapid decrease in COD with very little nitrification. Then after the COD concentration falls below 28 mg/l (as shown by the arrow), significant nitrification (greater than 0.25 mg/l NO_3-N) begins. Moreover, the curve with a COD_i equal to 74 mg/l does not reach a COD concentration until the bottom of the tower, and no

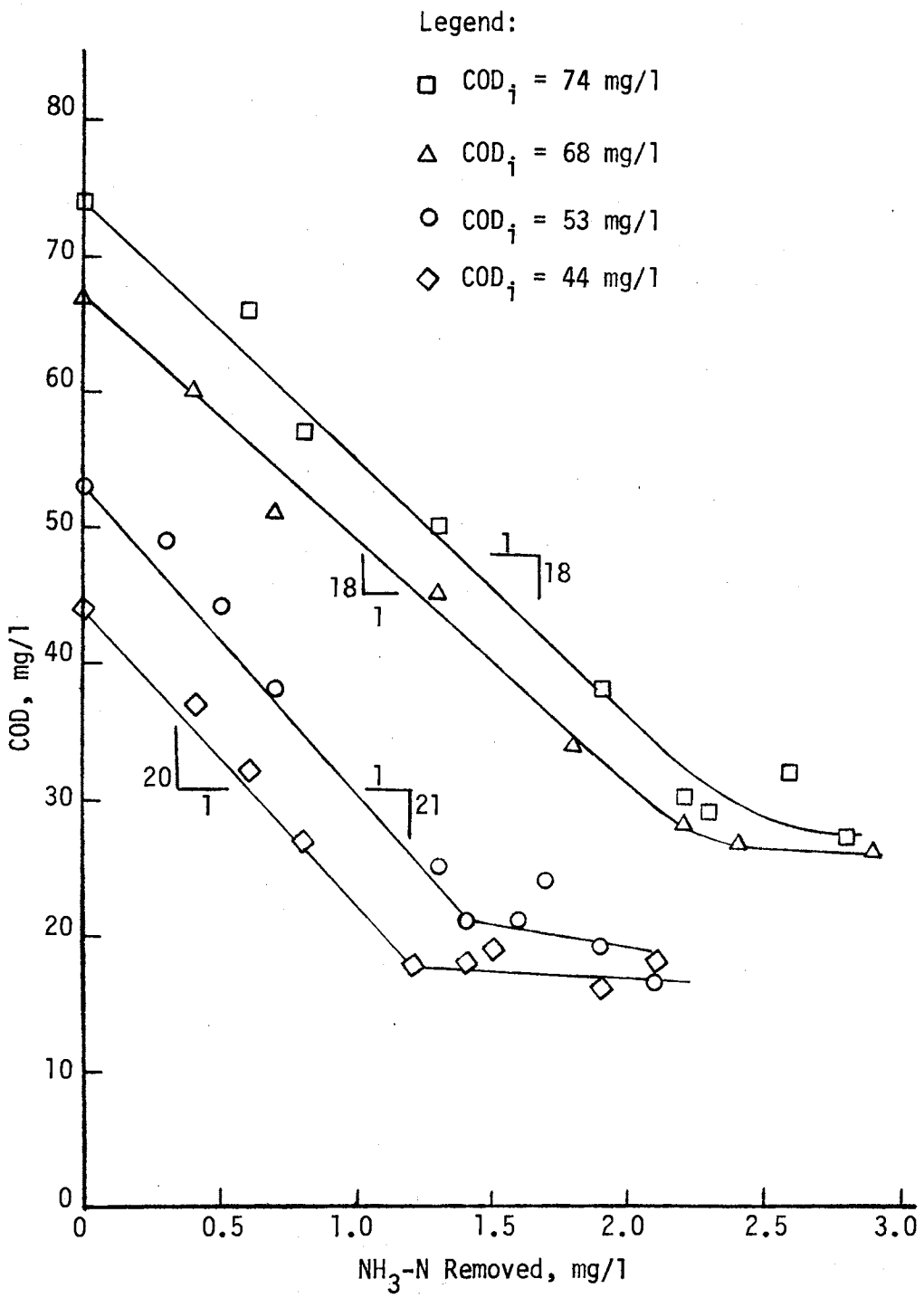

Figure 9. Composite COD vs NH_3-N Removed

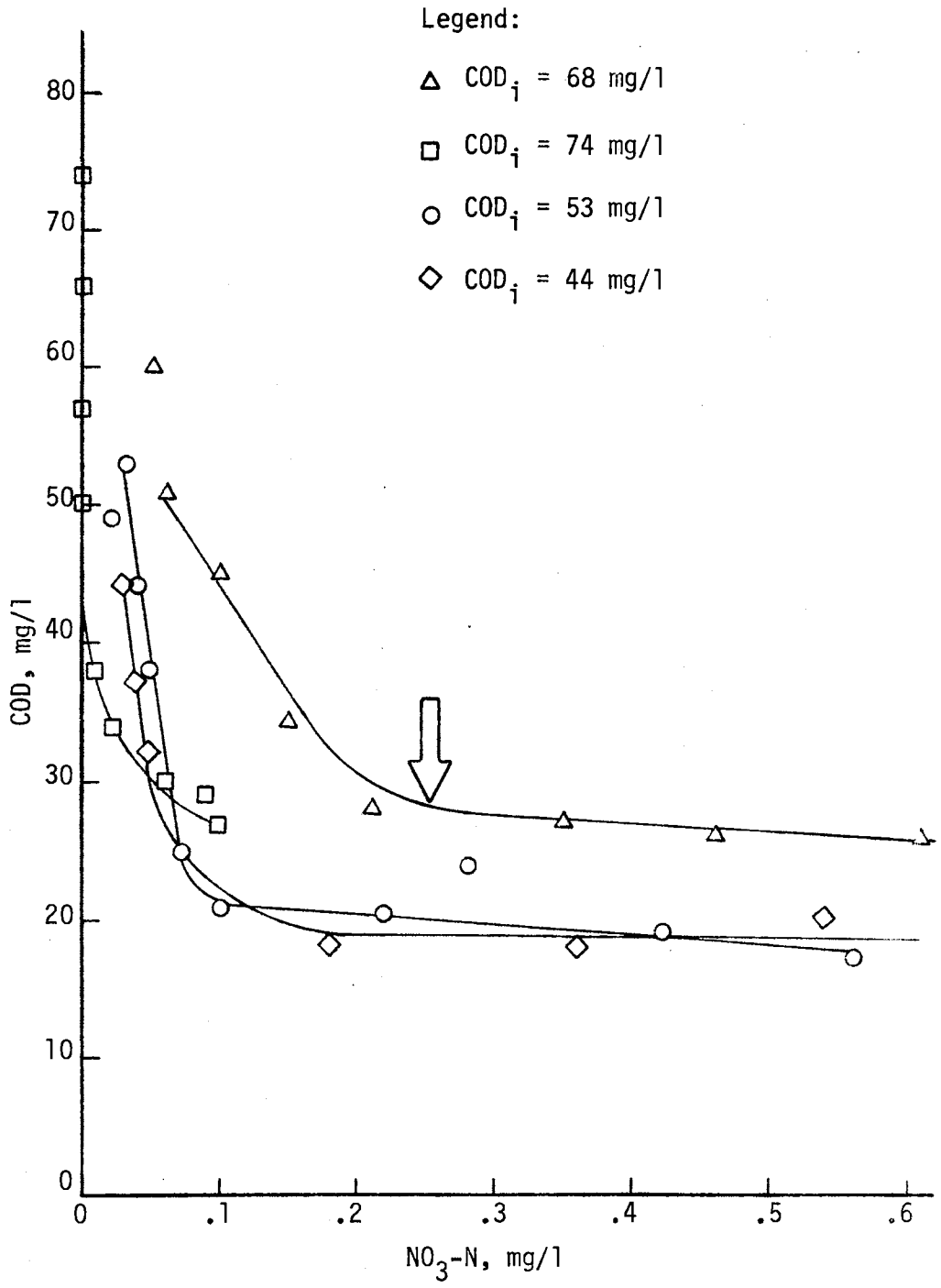

Figure 10. COD vs NO_3-N Formed

significant nitrification was developed.

B. Non-Steady State Conditions

An immediate organic shock load was placed upon the system on August 27, 1974. The influent COD concentration was increased suddenly from 44 mg/l to 83 mg/l. The shock was continued at an influent COD equal to 80 mg/l or more for 48 hours, and then returned to 47 mg/l. Steady state conditions before the shock have been shown by the fourth run of August 22, 23, and 24 (Figure 5).

Results from samples taken one hour into the shock load are shown by Figure 11. Here the COD and NH_3-N removals are in two phases, with zero order kinetics. Both removal curves have rate changes after the fifth foot of depth. The initial phase of the COD removal shows a rate of 11.0 mg/l/ft. This rate is 3.0 mg/l/ft higher than the rate found with an initial COD equal to 74 mg/l under steady state conditions (Figure 3). The second stage COD removal rate is a very low 0.125 mg/l/ft; however, the second stage now begins after the fifth foot. It is quite remarkable that the second stage beginning depth changed from after the fourth (see Figure 5) to after the fifth foot in the period of one hour under shock load conditions.

The first stage NH_3-N removal rate was quite high at 0.58 mg/l/ft, while the second rate was in line with steady state rates at 0.35 mg/l/ft.

No nitrification was detected during the first four feet of depth. The COD to NH_3-N removal ratio over this same portion of the tower was 18.96, an indication of heterotrophic growth. An increase in nitrification kinetics was observed during the fifth and sixth feet. Then a

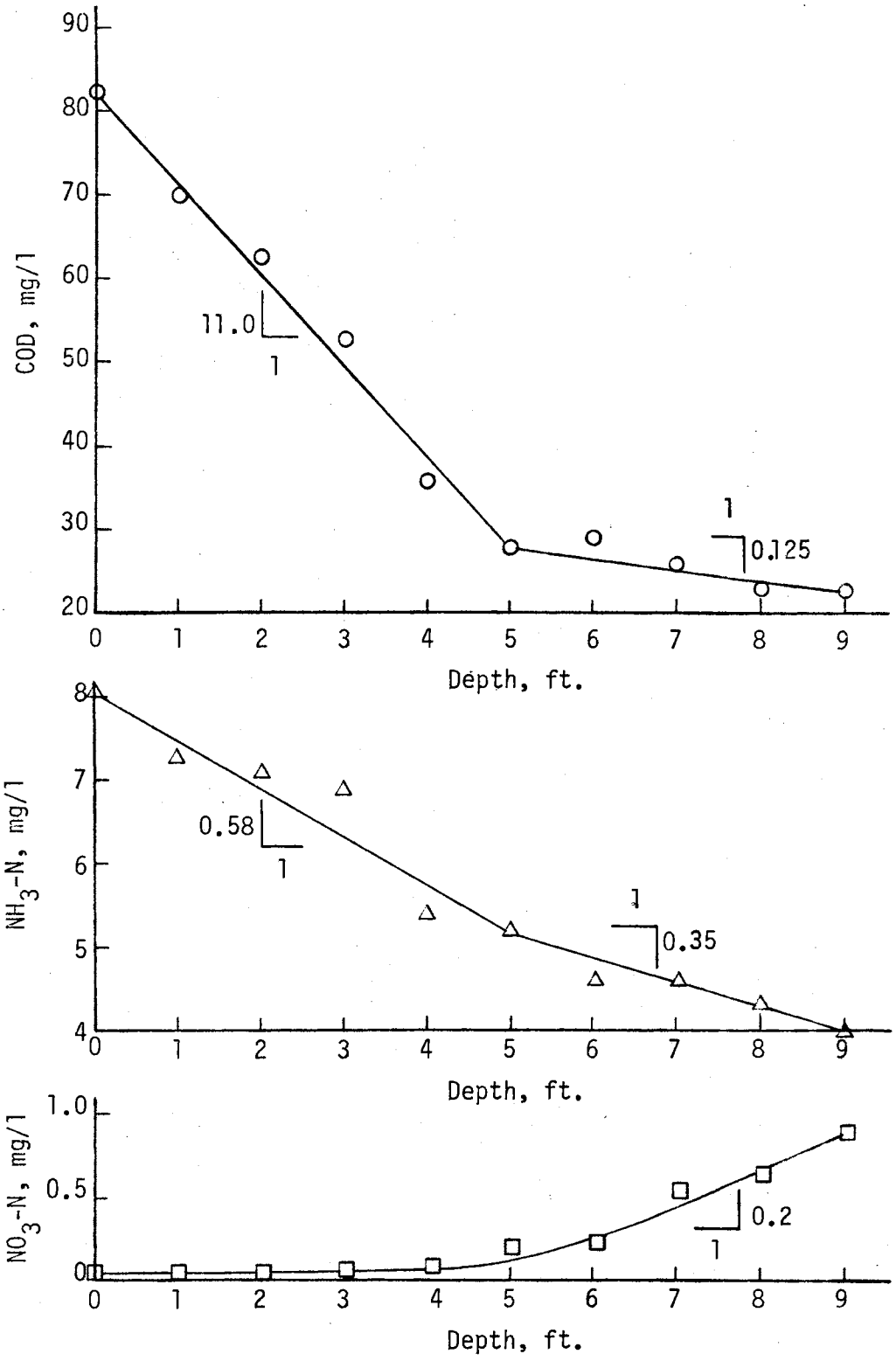

Figure 11. Parameters vs Depth, One Hour Into Shock Load, August 27, 1974. COD was increased From 44 mg/l to Approximately 80 mg/l

zero order increasing rate was observed over the last three feet at 0.2 mg/l/ft. This nitrification rate was the highest found thus far in the investigation. During the significant nitrification portion of the tower, the COD to NH_3-N removal ratio was a mere 0.357 mg/l/ft.

Some unusual results were observed at the sixth hour into the first shock, as shown by Figure 12. At this time, the first stage COD removal over the first four feet was 9.6 mg/l/ft. Then following two feet of kinetics change, the second stage removal rate was an extremely high value of 3.25 mg/l/ft. The previously highest value for this rate over the second stage was 1.75 mg/l/ft (Figure 3). Ammonia-nitrogen removal showed removal rates of 0.38 and 0.3 mg/l/ft for the first and second stages, respectively, with a change in removal kinetics after the fifth foot. The COD to NH_3-N removal ratio was an unprecedented high value of 25.3. While considering this ratio, one might expect that there was no nitrification during the first three feet of the tower due to "intense" heterotrophic growth. Following a kinetics transition during the fourth and fifth feet, nitrification followed zero order kinetics over the last four feet of depth. The rate of nitrification following these kinetics was a new high of 0.2 mg/l/ft. The COD to NH_3-N removal ratio for this depth was a medium value of 10.8. Therefore, there was probably some heterotrophic growth, but not a sufficient amount to hinder nitrification.

Figure 13 shows the results of samples taken 24 hours into the same shock load. The influent COD concentration was still above 80 mg/l. First stage COD removal now covered the first six feet of depth, one foot deeper than previous results. The first stage removal rate equal to 9.3 mg/l/ft did not vary much from the 9.6 mg/l/ft rate found

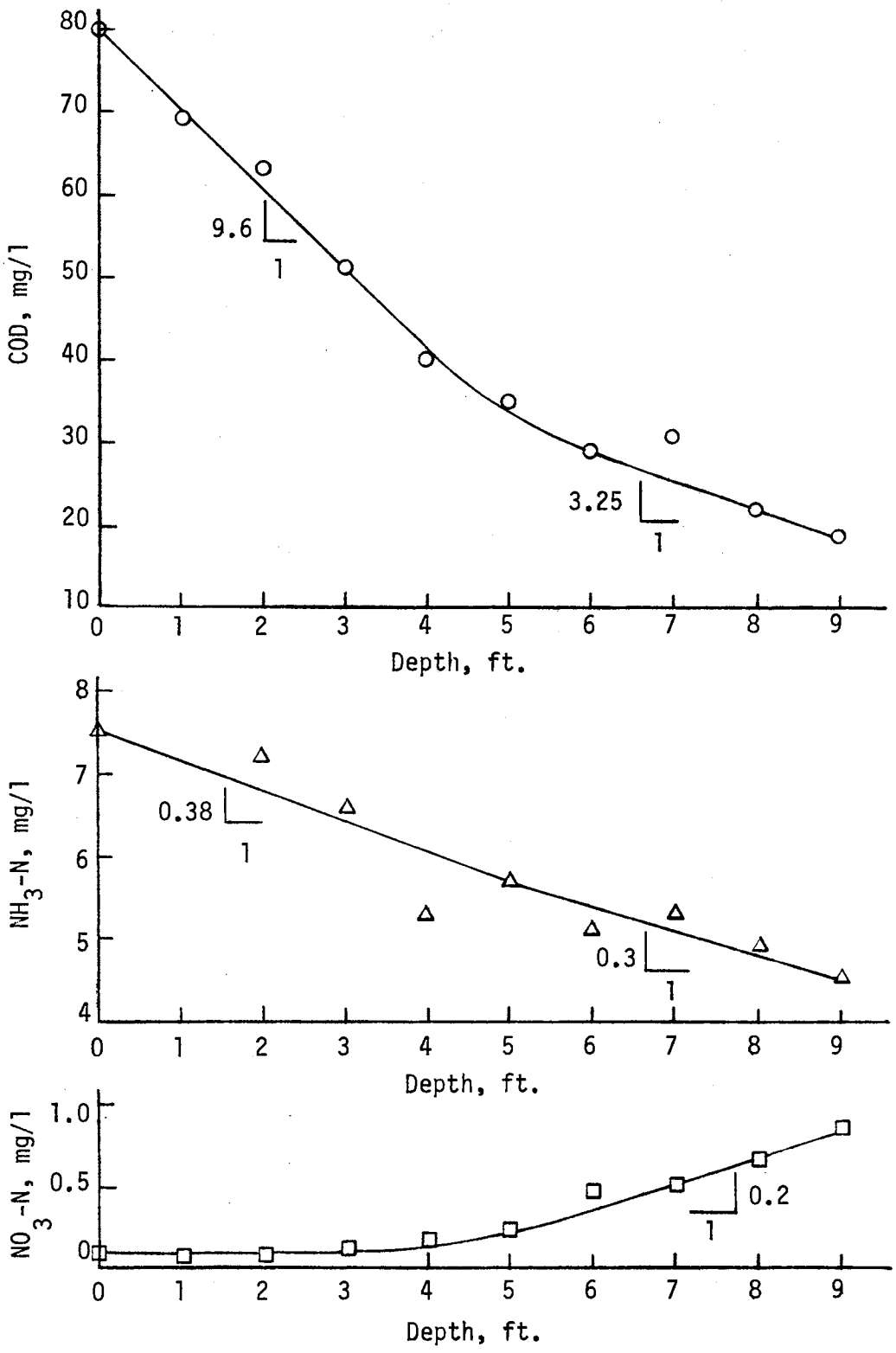

Figure 12. Parameters vs Depth, Six Hours Into Shock Load, August 27, 1974. COD, was Increased From 44 mg/l to Approximately 80 mg/l

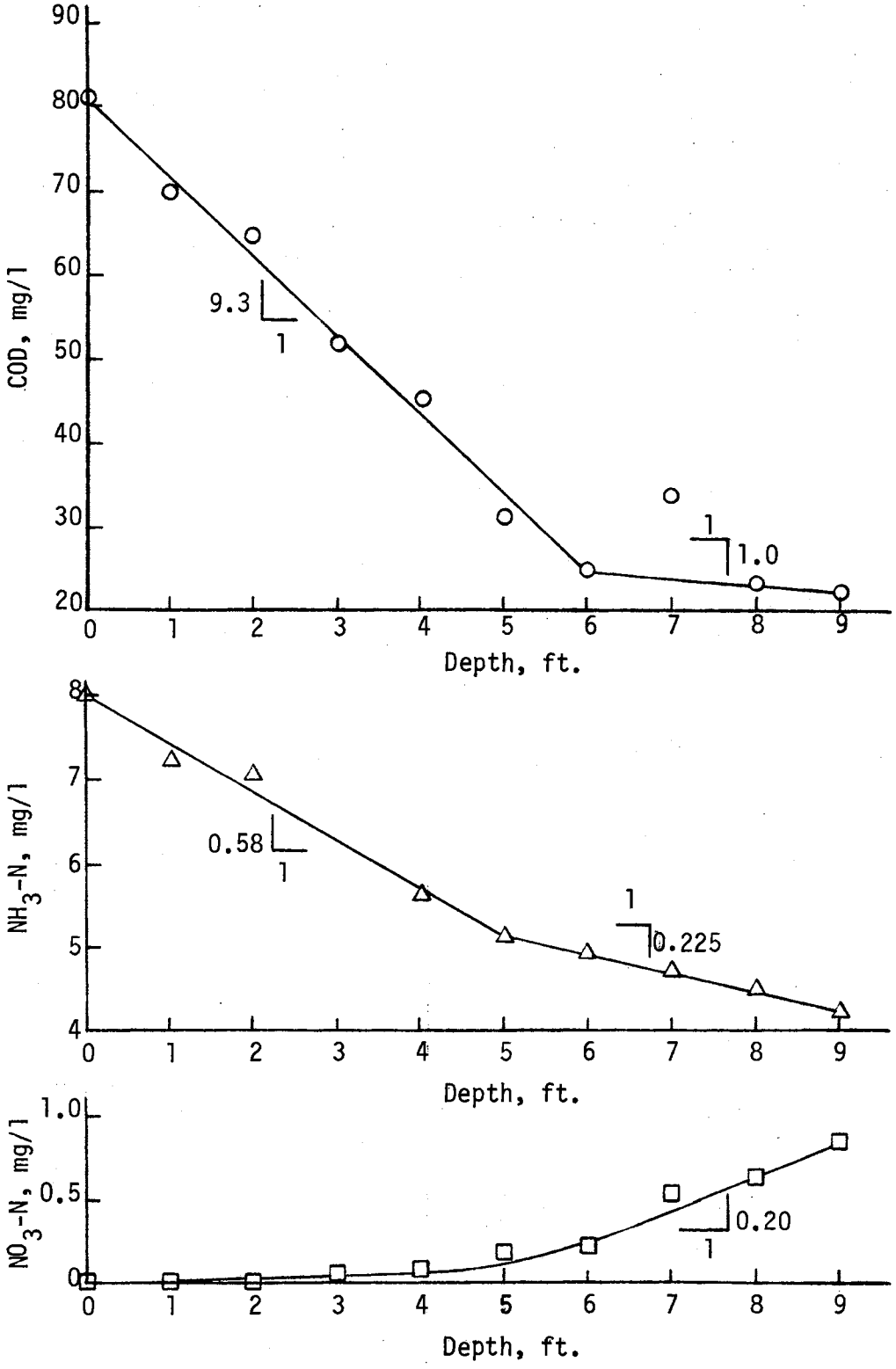

Figure 13. Parameters vs Depth, 24 Hours Into Shock Load, August 28, 1974. COD, was Increased From 44 mg/l to Approximately 80 mg/l

six hours into the shock. Following the change kinetics after the sixth foot, the second stage COD removal rate was 1.0 mg/l/ft.

Unlike COD removal, the NH_3-N first stage removal occurred over only the first five feet of depth. First and second stage NH_3-N removal rates were both median values at 0.58 mg/l/ft and 0.225 mg/l/ft, respectively. Again the ratio of COD and NH_3-N removals over their first stages was a high value--16.0--, and again there was no significant nitrification over these depths. A nitrification transition was found near the end of COD and NH_3-N first stage removals, i.e., during the fifth and sixth feet. Then another high nitrification rate of 0.20 mg/l/ft was found over the last four feet. The ratio of COD to NH_3-N removals over this depth was a low 4.44.

Figure 14 describes the purification effects at 48 hours into the shock, just before the shock was removed. The COD removal was again in two definite stages with a kinetics change occurring after the fifth foot of depth. First stage COD removal rate was a new high of 11.2 mg/l/ft with only a 0.33 mg/l/ft removal rate during the second stage. NH_3-N removal was similar to COD removal in that two definite stages were found with a kinetics change after the fifth foot. First stage removal rate was 0.7 mg/l/ft over the first five feet of depth. Second stage removal was according to zero order kinetics at a rate of 0.16 mg/l/ft. The ratio of COD to NH_3-N removal was again 16.0, as was the 24-hour first stage ratio (Figure 13). The 16.0 ratio is again an indicator of heterotrophic growth. Corresponding to this growth over the initial five feet (Stage I), there was no resulting nitrification. Only after the entire first stage did any sort of nitrification begin in the sixth foot (in earlier figures, nitrification began in the latter

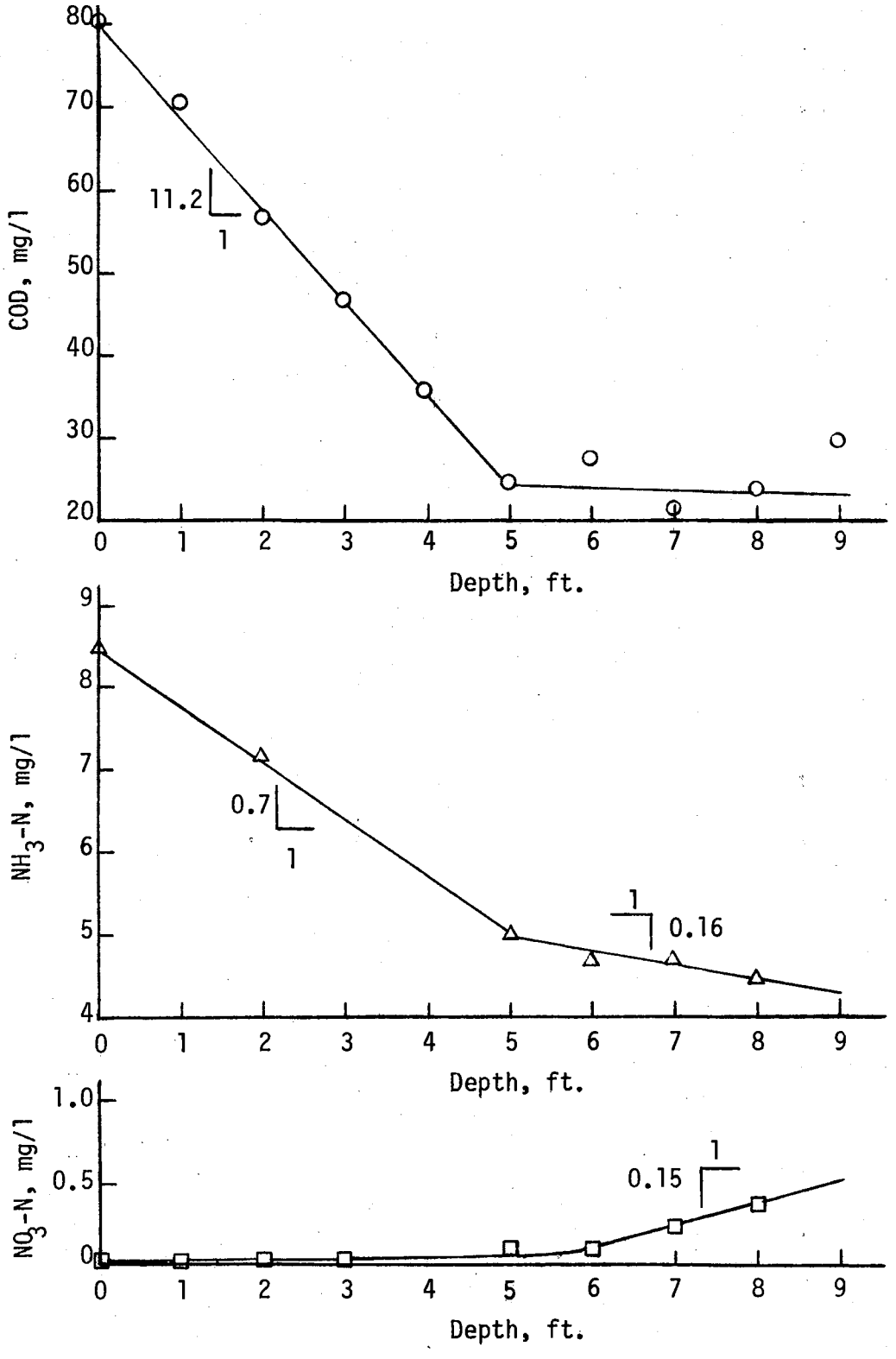

Figure 14. Parameters vs Depth, 48 Hours Into Shock Load, August 29, 1974. COD was Increased From 44 mg/l to Approximately 80 mg/l

portions of the first stage). Then after the transition, nitrification followed zero order kinetics at a high rate of 0.15 mg/l/ft over the last three feet of depth. The corresponding COD to NH_3-N removal ratio of 2.06 indicated that very little heterotrophic growth occurred.

Some two hours after the shock was removed, another set of data was found, as shown by Figure 15. The initial COD concentration was dropped from 81 m/gl to 47 mg/l. Still there were two stages of COD removal. The first stage removal rate was changed from 11.2 mg/l/ft back to a rate similar to the steady state rate before the shock at 8.25 mg/l/ft (see Figure 5). Also, the end of the first stage was shifted back to the original depth, i.e., after the fourth foot. Like the second stage COD removal before the shock, the after-shock second stage COD concentration remained constant at nearly the same concentration. Therefore, only two hours after the shock, the COD removal kinetics were similar to steady state removal kinetics before the shock. Similarly, the first phase NH_3-N removal rates corresponded to the earlier steady state rate; 0.425 mg/l/ft as compared to 0.325 mg/l/ft. However, the second phase NH_3-N removal was only one-half of the previous rate of 0.08 mg/l/ft.

The first stage COD to NH_3-N removal ratio was 19.4, very near 20.0, and a good indication of heterotrophic growth. As expected, there was no nitrification over the first four feet which are included in Phase I. Immediately after Phase I, the nitrification began in the tower during the fifth foot. Over the last four feet, zero order nitrification kinetics were observed at a rate of 0.09 mg/l/ft. This rate was considerably lower than the 0.2 mg/l/ft rate observed during the shock load, and significantly lower than the 0.14 mg/l/ft rate before the shock load, as shown by Figure 5. The nitrification rate over the last four feet

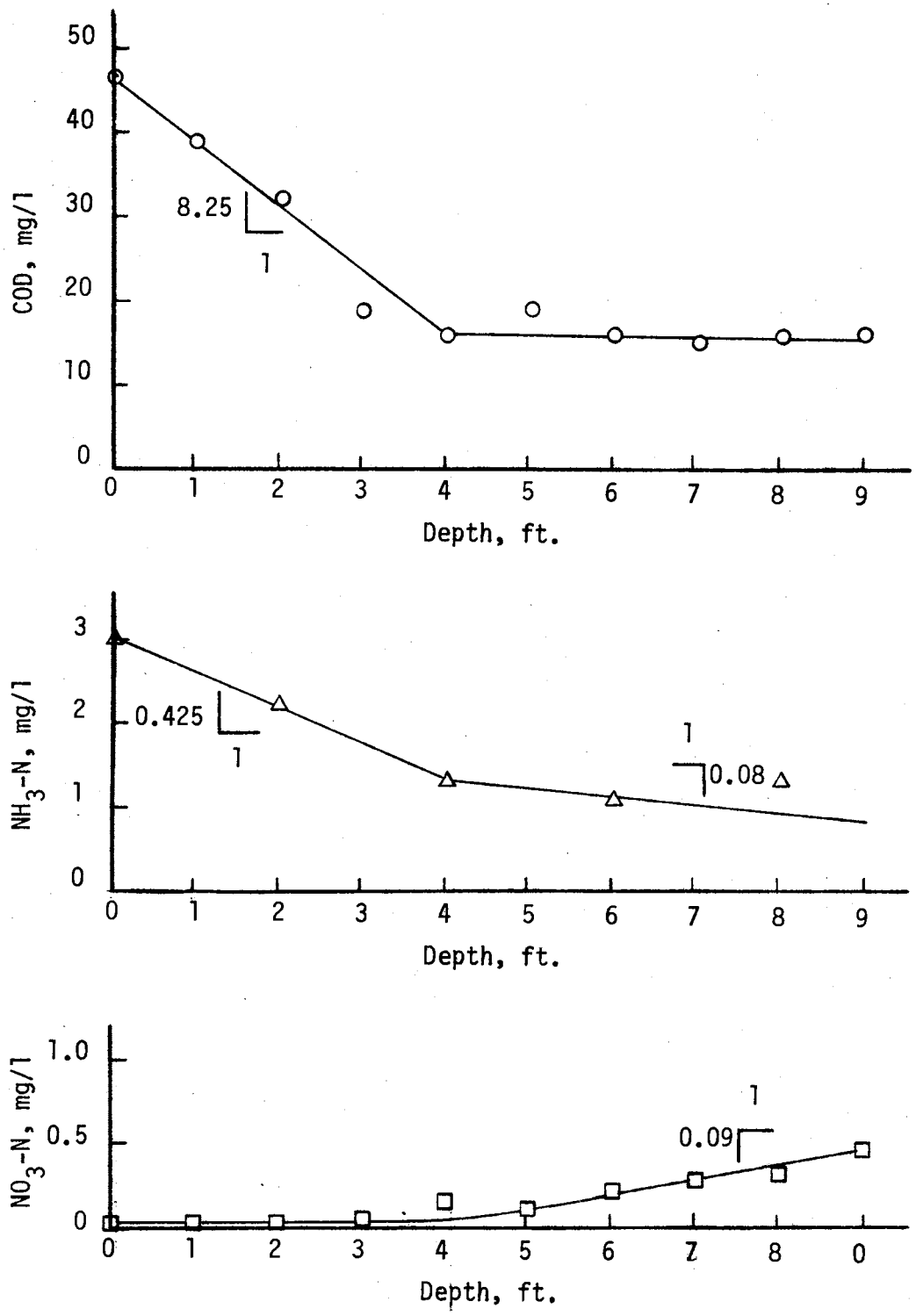

Figure 15. Parameters vs Depth, Two Hours After Release of Shock Load, August 29, 1974. COD_f was Reduced From 81 mg/l to 47 mg/l

nearly matches the 0.08 second phase NH_3-N removal rate. Therefore, the low nitrification rate accounts entirely for the low second stage NH_3-N removal rate.

Figure 16 shows the relationship between COD concentrations and nitrification at various times during and two hours after the shock load. All of the curves shown are in two phases, with definite changes in kinetics between the phases. During the first phase of the curves, there was little NO_3-N formation (nitrification), but a great deal of COD removal. Then after changes in kinetics, the curves exhibited the second phase with little or no COD removal and large increases in nitrification. As the curves indicate, all four of the shock load analyses began with essentially the same influent COD concentration. However, the first phase of each curve displayed an individual rate. Therefore, one may reason that nitrification did not follow the same COD removal kinetics through the first 48 hours of the shock; that is, the nitrification rates were not consistent with COD removals during the first phase of non-steady state conditions.

On all curves except the one at six hours, the COD concentration fell below 28 mg/l before significant (>0.25 mg/l NO_3-N) nitrification began. This was also observed under steady state conditions (Figure 10). Two hours after releasing the shock, the COD vs nitrification kinetics were very similar to steady state conditions before the shock load (see Figure 10, COD_i = 44 mg/l curve).

For seven days, from August 29 until September 5, the fixed-bed reactor was loaded at a COD concentration of 47 mg/l, which approximates the original steady state loading before the shock load. Then a second immediate shock load was placed upon the unit with a COD_i equal to 183

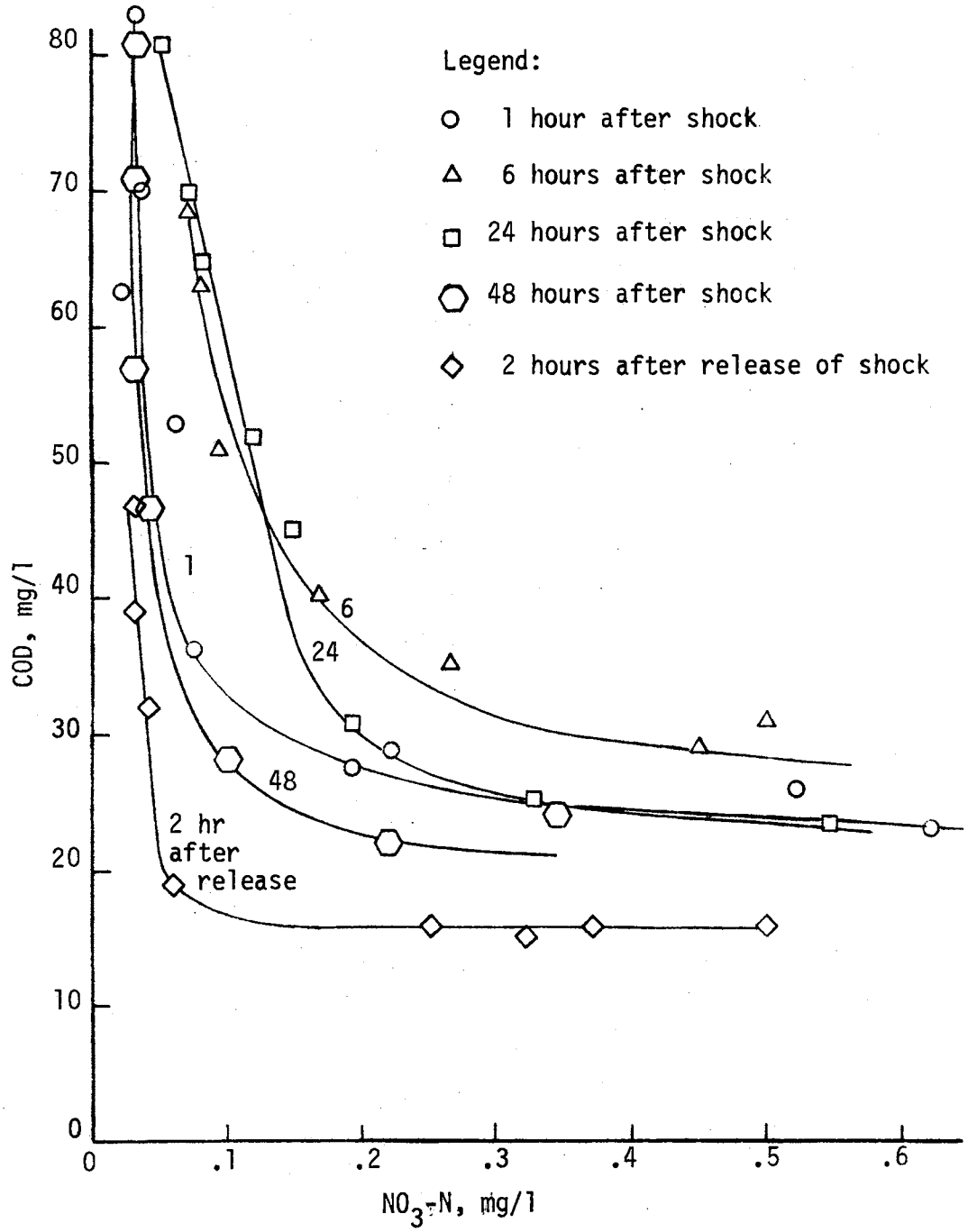

Figure 16. COD vs NO_3-N. Initial Shock Load

mg/l. This loading was continued for over 48 hours with an influent COD greater than 150 mg/l.

Figure 17 illustrates the results from samples taken six hours into the higher shock load. Again we find zero order kinetics for all of the parameters. The COD removal curve was in two phases with a change in kinetics occurring after the fifth foot. The Phase I COD removal rate was an extremely high value of 17.4 mg/l/ft. This value was much higher than the previously high rate of 11.2 mg/l ft found 48 hours into the first shock load (Figure 14). The second phase COD removal rate was another new high value of 8.0 mg/l/ft. This value was much greater than the high of 3.25 mg/l/ft for second phase COD removal found six hours into the first shock load (Figure 12).

Ammonia-nitrogen removal also occurred in two phases, with the kinetic change occurring at the same depth as COD removal change--after the fifth foot. First phase NH_3-N removal rate was a high value of 0.72 mg/l/ft, while the second stage rate was only 0.3 mg/l/ft. Nitrification did not occur at any depth at this time of the shock, since there was no observed increase in NO_3-N concentration. But the COD and NH_3-N removal curves were both in two phases--similar to the earlier shock load in which significant nitrification took place. Upon examination of the COD to NH_3-N removal ratios, we find ratios equal to 24.2 in the first phase, and 26.7 in the second phase. Therefore, heterotrophic growth occurred throughout all nine feet of the tower. Accompanying heterotrophic growth was a complete lack of nitrification. This occurrence is similar to results found under steady state conditions with COD_i = 74 mg/l (Figure 3). Here the COD and NH_3-N removals were in two phases, but only limited (0.1 mg/l NO_3-N) nitrification was

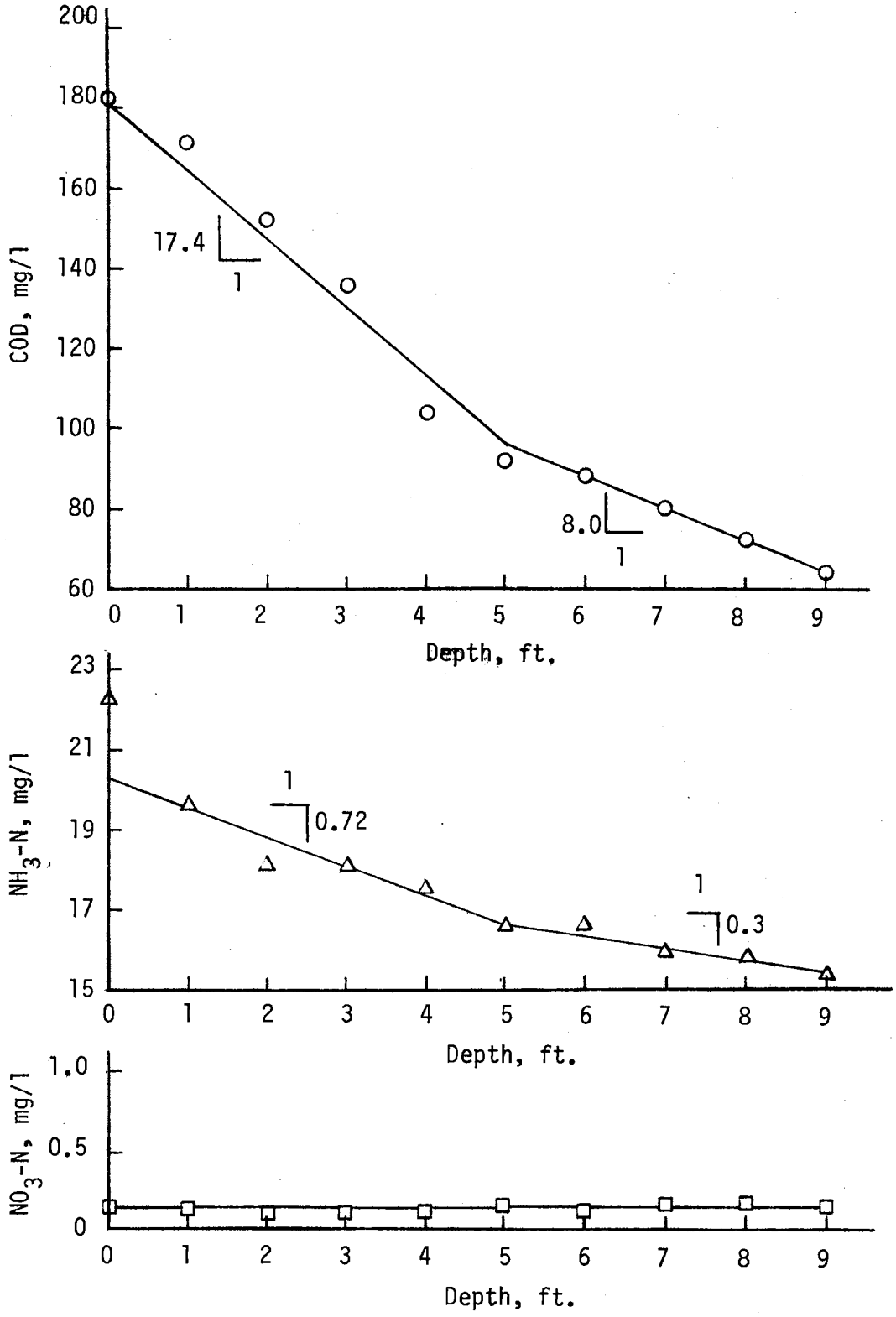

Figure 17. Parameters vs Depth, Six Hours Into Shock Load, September 5, 1974. COD_i was Increased From 47 mg/l to 183 mg/l

found. Similarly, the second phase COD to NH_3-N removal ratio was near 20.0, and implied heterotrophic growth.

After some 30 hours into the larger shock load, the nitrification was again completely disrupted, as shown by Figure 18. The COD and NH_3-N removals were now in single phases with removal rates equal to 11.3 and 0.45 mg/l/ft, respectively. The ratio of these rates was 25.1--an excellent indication of heterotrophic growth.

The relationship between the COD and NH_3-N removal ratio to the NO_3-N formation rate is shown by Figure 19. The data points from the second phase steady state results are used along with the single data point found 30 hours into the second shock load. This curve shows a definite relationship between an increase in COD and NH_3-N removal ratio to a decrease in nitrification rate. If the removal rate is greater than 5:1, then a nitrification rate less than 0.06 mg/l/ft can be expected. Also, the maximum nitrification rate occurs while there is a zero removal ratio, i.e., no decrease in COD concentration.

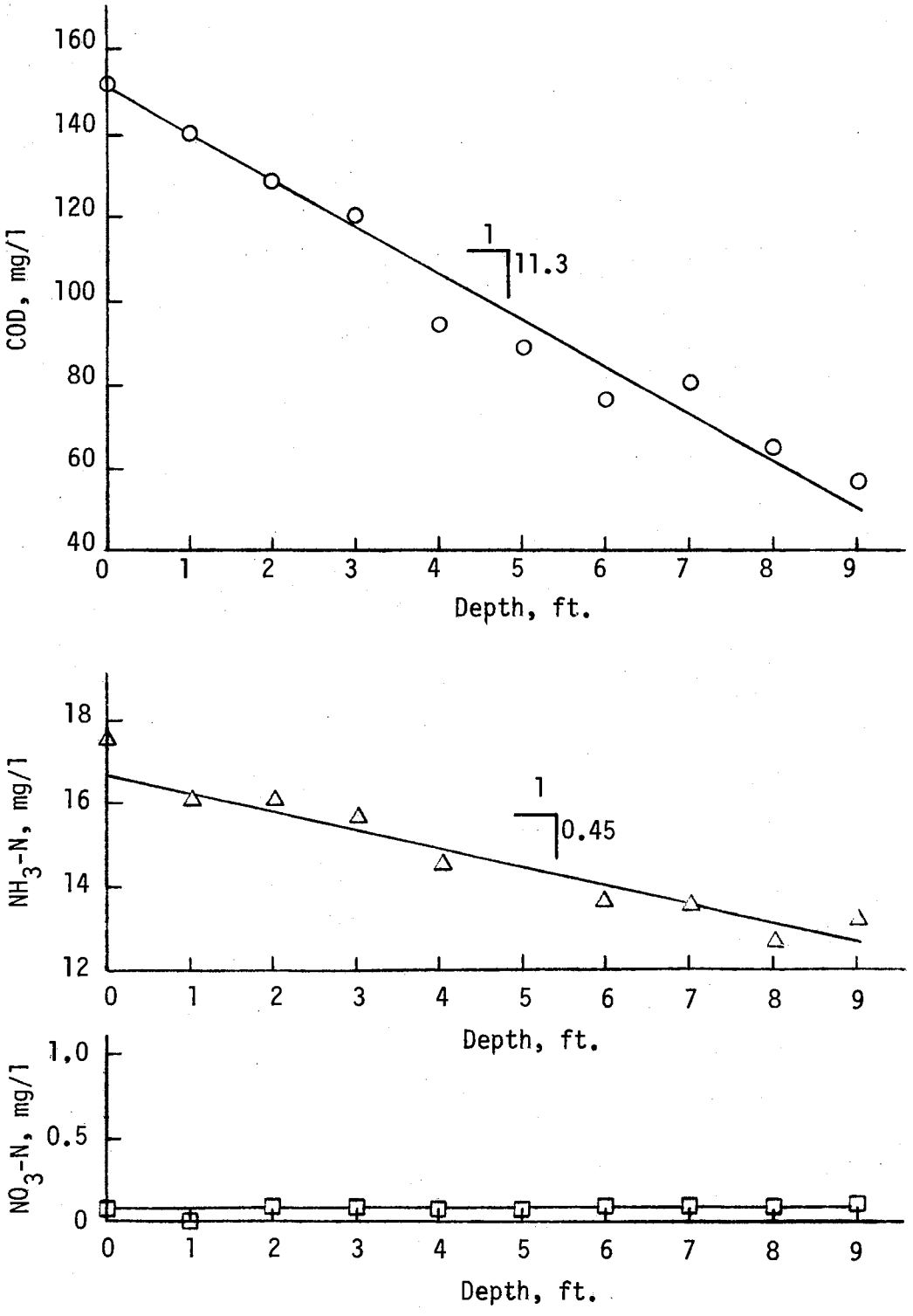

Figure 18. Parameters vs Depth, 30 Hours Into Shock Load, September 6, 1974. COD_i was Increased From 47 mg/l to Over 150 mg/l

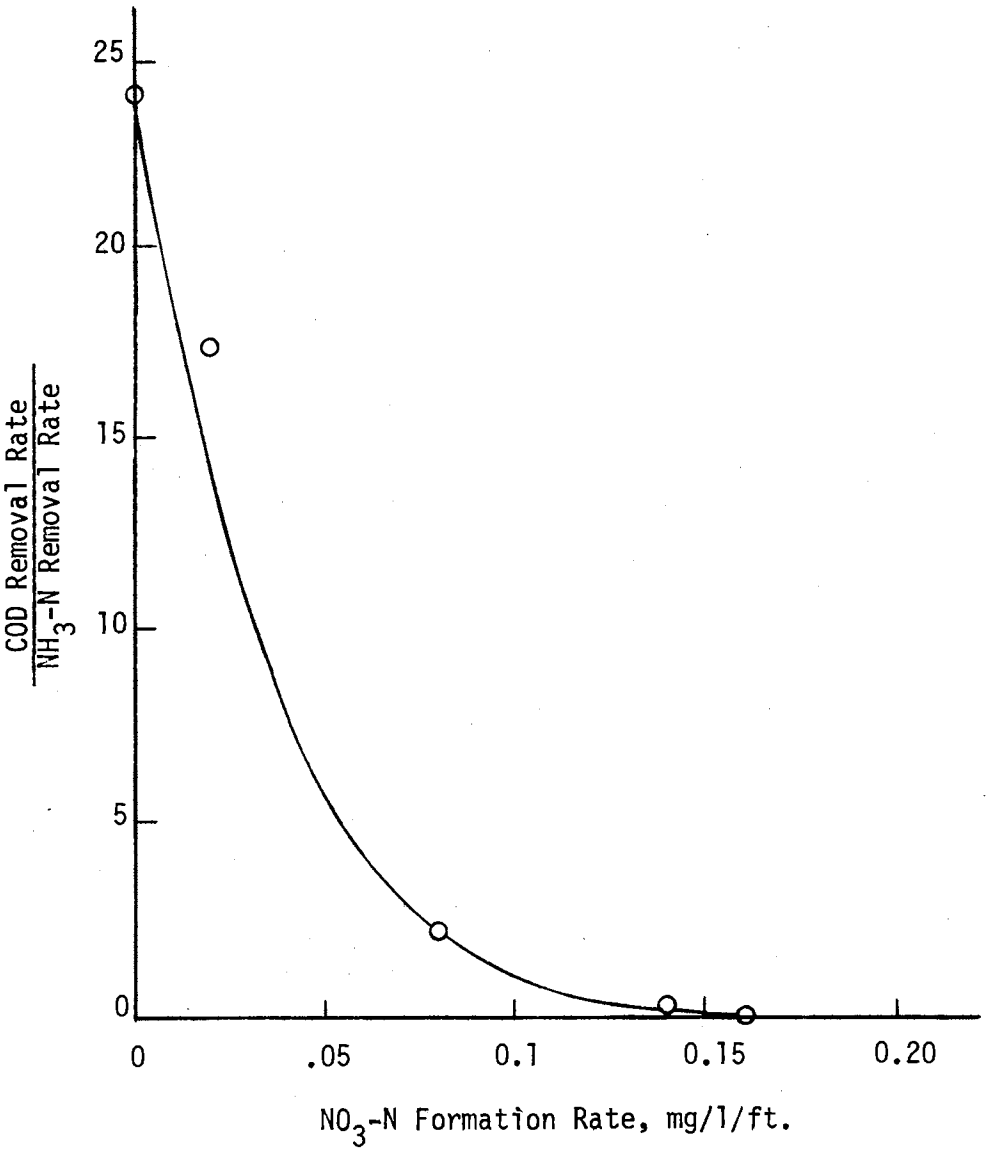

Figure 19: COD and NH_3-N Removal Ratio vs NO_3-N Formation Rate

CHAPTER V

DISCUSSION

All removal rates found by this investigation followed zero order kinetics. The reason this is important is that usually trickling filter removal follows first order. The probable explanation for the zero order phenomenon is the fact that only low influent loadings (less than 70 lb COD/1000 ft^3/day) were used. While using similar loadings, Stover (12) also presented his data as zero order kinetics.

The primary purpose of this study was to determine the chemical oxygen demand concentration after heterotrophic growth at which nitrification will commence. Steady state results shown by Figure 10 indicate that significant (greater than 0.25 mg/l/NO_3-N) nitrification began only after the COD concentration fell below 28 mg/l. This result was reinforced by the steady state run with an influent COD concentration of 74 mg/l. During this run, 0.1 mg/l NO_3-N was formed in the sixth and seventh feet of the reactor as the COD concentration fell to 30 mg/l. Then since the COD concentration did not fall below 28 mg/l, no further nitrification resulted. Non-steady state results shown by Figure 16 also lend partial reinforcement to this result. Significant nitrification at 1, 24, and 48 hours into the initial shock occurred at COD concentrations below 28 mg/l.

The 5-day biochemical oxygen demand with nitrification suppressed was also used to monitor the carbon level at which nitrification

commenced. Results from two steady state runs represented by Figures 4 and 5 show that significant nitrification began as the carbonaceous BOD_5 concentration was 15 and 7 mg/l, respectively. However, the COD concentration at this depth was only 20 mg/l. Therefore, some adjustment should be made to correspond the BOD_5 concentration to a COD concentration equal to 28 mg/l. By taking the difference in 20 and 28 mg/l and multiplying by a BOD_5/COD ratio of 0.8, the value of 6.4 mg/l is found. This value added to 15 mg/l, results in a BOD_5 of 21.4 mg/l.

This researcher feels that for a nominal design value, a carbonaceous BOD_5 equal to 20 mg/l should be used. That is, in order to expect significant nitrification to increase above a NO_3-N concentration of 0.25 mg/l, the carbonaceous BOD_5 should be reduced to a concentration of 20 mg/l.

In a Technology Transfer publication (4), the Environmental Protection Agency recommends that carbonaceous BOD_5 be removed to levels of about 50 mg/l. However, this researcher feels that this recommended level is too high. The introduction of a waste containing a carbonaceous BOD_5 of 50 mg/l into a biological tower used strictly for nitrification would probably (under steady conditions) result in the loss of the top three or four feet to nitrifying organisms. This loss in depth means the loss of 0.5 to 0.8 mg/l NH_3-N removal capacity.

Duddles, Richardson, and Barth (10) conclude that when operating at a low BOD_5 waste stream (15-30 mg/l) that high level nitrification (greater than 90 percent conversion) can be achieved in a 22.5-ft tower. However, these authors base their conclusions upon a study conducted with a waste streat at a BOD_5 range of 15 to 20 mg/l. They made no attempt to determine if the average TOC reduction of 6 mg/l within the

tower affected the nitrification kinetics. Certainly no basis exists to increase the effective influent level another 10 mg/l to 30 mg/l. Therefore, this researcher feels that the upper limit of their recommended BOD_5 influent concentration is a bit too high.

Present EPA secondary treatment requirements for municipal treatment plants calls for an effluent BOD_5 not to exceed 30 mg/l. One should use caution if he expects the effluent from a plant operating under these guidelines to have immediate nitrifying characteristics.

During all of the steady state runs, the COD removal occurred in two phases. In general, during the first phase, a large reduction in COD was found with no significant nitrification taking place. Then after the change in kinetics, a lower COD removal rate was accompanied by zero order nitrification rates. The exception to this trend was the run conducted with an influent COD equal to 74 mg/l (Figure 3). Here, the second stage COD and NH_3-N removal rates were both low. Therefore, one might expect significant nitrification to develop during the second stage. However, the ratio of the COD and NH_3-N removal rates was 17.5:1, near the 20:1 ratio of heterotrophic growth. One may conclude, then, that heterotrophic growth was taking place, precluding significant nitrification.

Also during the second shock load, a definite change in COD and NH_3-N removal kinetics was observed after six hours (Figure 17). At this time, two removal rates were found on both the COD and NH_3-N curves. By observing the two distinct phases, one would expect that nitrification would occur in the second phase. However, the ratio of COD and NH_3-N removal rates was 26.7:1--an excellent indication of heterotrophic growth. In direct support, there was no nitrification

during the second phase, as shown by the NO_3-N curve. Therefore, the presence of a two-stage COD or NH_3-N removal curve with a definite intermittent change in kinetics does not always predict nitrification. If the ratio of COD and NH_3-N removal rates is near 20:1, then heterotrophic growth is indicated and nitrification is precluded.

A definite relationship exists between the COD and NH_3-N removal ratios and nitrification. The lower the ratio, the higher the nitrification. If no COD is removed and the ratio is zero, the nitrification is at its maximum. The studies by Stover (12) showing the disruption of nitrification by heterotrophic growth are certainly reinforced by this relationship.

Another important factor is the depth at which nitrification began. The first steady state run resulted in significant nitrification beginning in the sixth foot, as shown by Figure 2. Then by increasing the influent COD concentration to 74 mg/l, the nitrification was disrupted and significant nitrification did not develop (Figure 3). During the next run five days later, the influent COD concentration was dropped to 53 mg/l, and significant nitrification developed again in the seventh foot. Again the influent COD was lowered during the next run; this time to 44 mg/l. Now significant nitrification developed in the fifth foot. Thus, significant nitrification was achieved, shut off, and then the beginnings of significant nitrification brought up the tower in two steps. All of this was achieved by controlling the influent COD concentration.

The rise of nitrification in the tower against the flow of wastewater without futher seeding seems to indicate the existence of nitrifiers among heterotrophic organisms. But the nitrifiers did not begin

nitrification until the growth of the heterotrophs was significantly curtailed, as shown by the COD and NH_3-N removal ratios.

Heukelekian (6) proved the existence of nitrifying flora among heterogrophs in high-rate trickling filters where only a 0.7 mg/l NO_3-N was being produced. These flora were not heavily nitrifying until after the film was scraped from the medium and placed in a liter of sewage and aerated for 24 hours. Therefore, nitrifiers may exist in the biological film while carbonaceous removal takes place, without nitrifying. Then as the environmental conditions become more favorable, nitrification takes place. Nitrification may be shut off by carbonaceous growth and then begin again after a reduction in carbonaceous growth. One very important question appears from these results. What happens to the nitrifying microorganisms while they are not nitrifying under carbonaceous growth conditions? Possibly their growth rates decrease or the organisms fall into a dormant state. However, only two hours after the initial shock load had ended, significant nitrification was again attained in the seventh foot of depth, as shown by Figures 14 and 15. Thus, this researcher was led to believe that the nitrifiers in the seventh foot were still using energy during their period of non-nitrification.

Another important question was raised by these results. What aspect of heterotrophic growth shuts off nitrification? As discussed earlier, there is a definite relationship between heterotrophic growth as shown by the COD and NH_3-N removal ratio and nitrification rate (Figure 19). The relationship shows a rapid increase in nitrification rate below a ratio of 5:1. Therefore, the early beginnings of heterotrophic growth inhibits nitrification. Possibly a metabolic intermediate from

heterotrophic metabolism causes the inhibition. Perhaps some of the short carbon chain refractory compounds remaining after the long chain carbon compounds are broken during purification could cause the inhibition.

The maximum NO_3-N formation rate as shown by Figure 19 exists when there is no heterotrophic growth, i.e., when COD removal has ended. The highest nitrification rate shown by the figure is 0.16 mg/l/ft. However, nitrification rates equal to 0.20 mg/l/ft were observed during the initial shock loading conditions (Figures 12 and 13). These data should be of particular interest to the design engineer who must design the depth of tower required for a certain degree of removal. However, this rate must be qualified by 1) the temperature of the wastewater, 2) pH, 3) presence or absence of inhibitors, 4) media configuration including specific surface area, 5) ammonia nitrogen loading rate, and 6) COD concentration which determines if carbonaceous growth will occur.

Figure 7 shows that the removal of NH_3-N in a combined synthesis-nitrification fixed-bed reactor occurs in two phases. During the first phase, the NH_3-N is used by heterotrophic microorganisms for synthesis of new cells. The observed NH_3-N removal rates varied from 0.3 mg/l/ft to 0.44 mg/l/ft. During the second or nitrification phase, the NH_3-N removal rates were observed from 0.1 mg/l/ft to 0.3 mg/l/ft. As seen by these results, NH_3-N removal by nitrification is much less effective than NH_3-N removal by synthesis.

If at some future time, wastewater treatment plant operators could adjust the influent waste stream COD:NH_3-N ratio to nearly 20:1, then the NH_3-N could be efficiently removed by synthesis. However, this method would be quite difficult to operate and not economically feasible

at this time. According to Sawyer (2), and McCarty (3), nitrification is the best method for completing NH_3-N removal requirements at this time.

During the shock loading conditions, it was observed that the COD removal rate was increased over the rate found with similar loading conditions under steady state (see Figures 3 and 11). Without the increased COD removal rate, there would have been less nitrification within the biological tower, since the critical COD concentration would have occurred at a lower depth.

CHAPTER VI

CONCLUSIONS

1. There exists a definite COD concentration at which nitrification will begin in a biological tower.

2. Nitrification did not occur in the presence of heterotrophic growth.

3. Ammonia-nitrogen removal by synthesis of heterotrophic microorganisms is more effective than ammonia-nitrogen removal by nitrification.

4. COD removal rates can increase under shock loading conditions.

CHAPTER VII

SUGGESTIONS FOR FUTURE STUDY

1. Study nitrification rates in a biological tower while using varied ammonia-nitrogen loading rates and environmental conditions.

2. Study the effects of temperature upon nitrification.

3. Study the effects of other types of shock loads upon nitrification.

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